

**MODELING AN ENDANGERED SPECIES IN AN URBAN LANDSCAPE:
FOUNTAIN DARTER (*Etheostoma fonticola*) SURVIVAL IN THE UPPER SAN
MARCOS RIVER, HAYS COUNTY, TEXAS**

A Thesis

by

LEANN IRENE WILKINS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2009

Major Subject: Wildlife and Fisheries Sciences

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Approved by:

Co-Chairs of Committee,	William E. Grant
	Miguel A. Mora
Committee Member,	Patricia K. Smith
Head of Department,	Thomas E. Lacher, Jr.

May 2009

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ABSTRACT

Modeling an Endangered Species in an Urban Landscape: Fountain Darter (*Etheostoma fonticola*) Survival in the Upper San Marcos River, Hays County, Texas. (May 2009)

Leann Irene Wilkins, B.S., University of Miami

Co-Chairs of Advisory Committee, Dr. William Grant
Dr. Miguel Mora

To accommodate for human population growth along the Texas I-35 corridor, land is becoming increasingly urban and decreasingly pervious, modifying the infiltration and runoff rates in the Edwards Aquifer, especially to its spring fed Upper San Marcos River (USMR). Contaminants like heavy metals and organic chemicals can accumulate on impervious surfaces and with runoff, enter into the USMR at potentially harmful levels. The objective of this study was to determine how the population of an endangered Edwards Aquifer species, the fountain darter (*Etheostoma fonticola*), might respond to potential water quality changes associated with urbanization. I developed a stochastic, sex and stage-structured population dynamics simulation model that represents the relationships between urbanization, springflow variations, contamination levels, and natural history of the fountain darter.

Future fountain darter population trends (2008–2040) were simulated under 10 treatments of nine scenarios. A simulation scenario (n=50) corresponded to one of three variations of springflow (random, high and low flow) and one of three variations in percentage of runoff entering the river (100, 50 or 30). The 10 treatments were variations on water quality: uncontaminated (1), contaminated by Cu (2), Zn (3), Cd (4), Cr (5), polycyclic aromatic hydrocarbons (PAH) (7), bifenthrin (8), carbaryl (9) and dicamba (10) and an additive affect of Cu, Cr, Cd, and Zn (6).

Simulating ideal conditions, the average darter population from 2008-2040 was 54155 ± 2969 (mean \pm SE) individuals. Contaminant treatments that caused a significant

($p < 0.001$) decline in the population by 2040 under 100% runoff conditions were the all metal (650 ± 640), Cu (3141 ± 265), PAH (4621 ± 475), Zn (6169 ± 5406), and Cd (27987 ± 6751) scenarios. With 50% runoff, the all metals (15740 ± 5455), Cu (16815 ± 6263), PAH (19675 ± 995), and Zn (15585 ± 3097) treatments simulated significantly lower populations ($p < 0.001$). At 30% runoff, Cu (23976 ± 6787), the all metal (25853 ± 7404) and PAH (28167 ± 1194) treatments decreased the population significantly ($p < 0.001$). Over all scenarios, copper, zinc and PAHs caused $>50\%$ decline in the population. Assuming 100% or 50% of all San Marcos sub-basin runoff is directly entering USMR, there could currently be levels of Cu, Zn, and PAHs higher than what darters can withstand.

DEDICATION

For the past:

Ace Wilkins and *Jo Voss*,
for opening my mind with a rabbit and hikes in Evergreen.

&

To the future:

Keith Cody Wilkins,
the sky is your limit.

ACKNOWLEDGEMENTS

This would not have been possible without the direction, assistance and expertise of my committee: Dr. William Grant, Dr. Miguel Mora, and Dr. Patricia Smith. Thank you for your valuable feedback and insight as well as for your assistance in editing the final product.

The United States Geological Survey funded this research. Thanks to them for supplying demographic, land use and hydrologic data vital to the development of the model.

Also, the first hand experience of Patrick Connor, Tom Brandt (US Fish and Wildlife Service) and Gordon Linam (Texas Parks and Wildlife Department), was not underestimated. Thank you.

Thanks to the previous students who gave me advice along the way and to my friends and family for the never-ending encouragement. Finally, to JR who was my anchor of perspective through this research. You deserve special thanks for your support, patience and understanding while I worked to complete this project.

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CHAPTER I

INTRODUCTION

Background: Edwards Aquifer and land use changes

Can we have the quantity and quality of water needed to support the demands of the future without compromising the integrity of aquatic ecosystems? The answer to this question is important as cities continue to accommodate for the rising human population's demand for water. Much of the water used comes from surface sources such as streams, rivers, reservoirs and lakes as well as underground sources such as aquifers. One of the most unique is the Edwards Aquifer in south-central Texas (Fig. 1) which supports the municipal, agricultural, industrial and recreational needs of nearly 2 million people (Earl and Wood, 2002) including the San Antonio metropolis. Although it is the sole-water source in the area, it is a rechargeable karst system that is world recognized for its ability to support aquatic species of flora and fauna; many endangered or threatened (Lindgren et al., 2004). Should the quantity or perhaps the quality of water become compromised, these endemics, supported by the aquifer's many springs, might be in peril (Chen et al., 2001; Saunders et al., 2001; Van Sickle et al., 2004).

The aquatic systems that contain such species are supported by the groundwater that is recharged in the southern Edwards Plateau and flows through the porous and permeable limestone, undergoing purification as it flows east and northeast to be discharged at the surface via springs (Longley, 1981). Two such springs are the Comal and San Marcos, known for their water quality and size, as they are the two largest freshwater springs in Texas, respectively. The aquifer's constant groundwater flow into the springs creates stability for aquatic habitats at these headwaters (Groeger et al., 1997). The consistent conditions of the springs and their associated river can be characterized by an average water temperature of 22°C with variability increasing downstream, a slightly basic pH of 7.2-7.8, low mean turbidity levels (1.9 nephelometric turbidity units), and stable ammonium (1-30 µg/L), nitrate (1500-1700 µg/L) and salinity

This thesis follows the style of Ecological Modelling.

levels (Groeger et al., 1997; Hubbs, 2001; Saunders et al., 2001; Earl and Wood, 2002). The consistency in temperature, water quality and nutrients has led to the occurrence of species found nowhere else in the world.

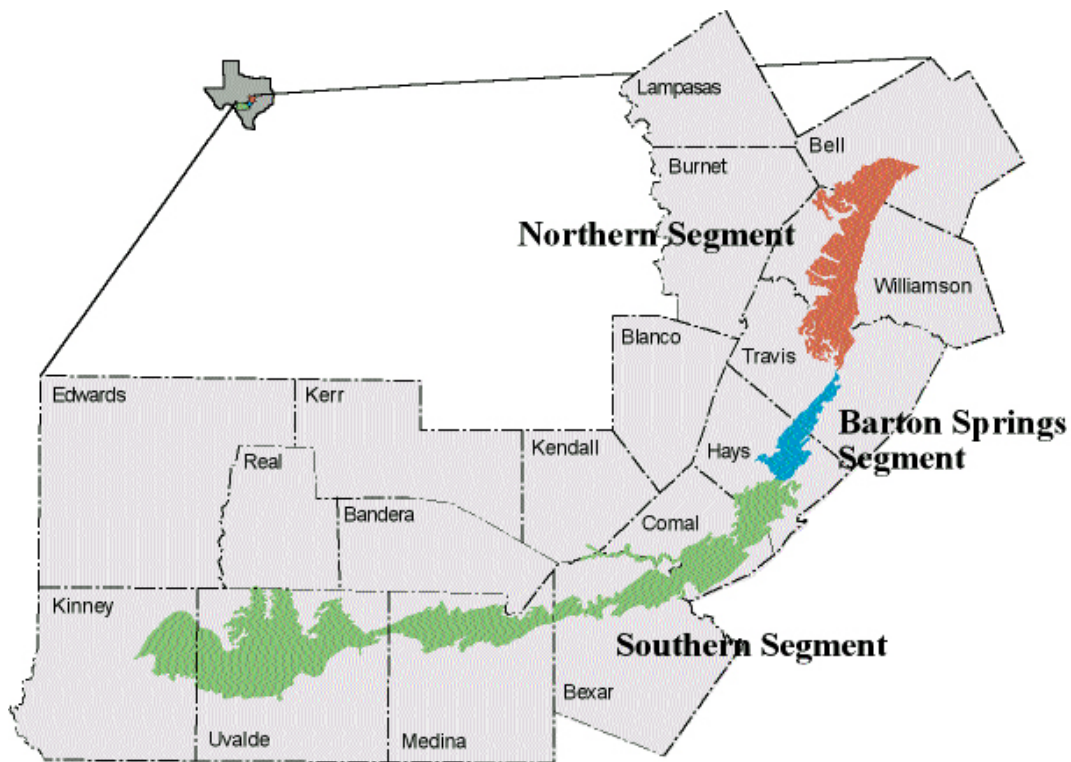


Fig. 1. Counties comprising the Edwards Aquifer in south-central Texas (Eckhardt, 2007).

The aquifer and its supporting springs and rivers support seven endangered and one threatened species: the San Marcos salamander (*Eurycea nana*), the Comal Springs dryopid beetle (*Stygoparnus comalensis*), the Comal Springs riffle beetle (*Heterelmis comalensis*), the fountain darter (*Etheostoma fonticola*), the Peck's cave amphipod (*Stygobromus pecki*), the San Marcos gambusia (*Gambusia georgei*), the Texas blind salamander (*Typhlomolge rathbuni*) and Texas wildrice (*Zizania texana*) (USFWS, 1995). For state and federal agencies in charge of natural resource protection, managing

for the demands of an increasing human population as well as striving to protect unique species into the future is of great concern. To assess how all endangered species within the Edwards Aquifer might fair into the future is beyond the scope of this assessment, therefore I chose one of the seven species of concern, the fountain darter. The fountain darter is an indicator of the aquifer, as it generally is the first to be affected by low flow conditions (Votteler, 1998). They require steady springflow, minimal water temperature variability, appropriate vegetation composition, and excellent water quality to survive. All of which can be potentially compromised as the city of San Marcos continues to grow.

Although there is natural variation in water condition, the quality of urban runoff and non-point source discharges are likely to change as the human population grows around these springs. A feature of urbanization is land use change and increase in impervious surfaces, area that resists infiltration of water to the soil. Bridges, streets, highways, rooftops, sidewalks, and even compacted soil are types of impervious surfaces in urban environments (Arnold and Gibbons, 1996). The percentage of impervious surface area correlates to the degree of urbanization (Schueler, 1994; Brabec et al., 2002) and the degree of urbanization is related to an area's population (Arnold and Gibbons, 1996). Therefore, in the San Marcos region, where the population is projected to increase 3.7 times its 2000 census level (~31,000 to ~130,000 individuals) the impervious area of the city limits is expected to also increase over the next 30 years (USGS, 2007).

The relationship between human growth and decrease in pervious area is important because there is a direct relationship between impervious surface cover and pollution levels (Arnold and Gibbons, 1996; Miltner et al., 2004). This is a concerning truth considering that pollutants settle on roads, highways, rooftops and parking lots and are then introduced into the waterways when it rains, making runoff more than just rainwater excess. As a nonpoint source of pollution, runoff can potentially decrease water quality in a drainage area (Van Sickle et al., 2004). As the runoff travels over impervious surfaces, it becomes a vector for the pollutants to move directly or indirectly

into aquatic systems (Brezonik and Stadelmann, 2002). It is not surprising that aquatic biological diversity is negatively correlated to percentage of impervious surface (Wang et al., 2001). Chemicals may be dissolved or adsorbed to sediment molecules in runoff, but if persistent, once in the surface waters will accumulate over time and become toxic, threatening the aquatic life.

Many studies have assessed the chemical composition of urban and road runoff (Muschack, 1990; Wu et al., 1998; Davis et al., 2001; Brezonik and Stadelmann, 2002; Kim et al., 2005). Contaminants that are found at levels often above aquatic life criteria include inorganic and organic chemicals, such as heavy metals, petroleum based hydrocarbons and pesticides. The most frequently detected metals in urban streams are zinc, copper, cadmium, lead, chromium, and nickel (Muschack, 1990; Paul and Meyer, 2001). The hydrocarbons of concern are pyrene, fluoranthene and phenanthrene, as they account for the majority of PAH toxicity in extracted sediments (Boxall and Maltby, 1997). In a study of eight urban streams around the U.S., Hoffman et al. (2000) reported that 97 percent of their samples contained at least 1 herbicide and 89 percent at least one insecticide. In fact, seventy to ninety percent of households in the United States use pesticides for lawn care and insect control (Paul and Meyer, 2001).

After a thorough literature review of the urban contaminants most often washed into our urban streams, I determined that I would model 4 metals and 4 organics as representative of the urbanization within the San Marcos sub-basin. For metals, I modeled the effects of zinc, copper, chromium and cadmium. I selected phenanthrene to represent polycyclic aromatic hydrocarbons and the other three organics (all pesticides) are dicamba, carbaryl and bifenthrin. All eight contaminants are present in urban applications and pose a potential for toxicity to aquatic organisms like the fountain darters (Chapters III and IV).

Study area

The Edwards Aquifer is approximately 282 km long and 8 to 64 km wide (Longley, 1981) and comprises the majority of Uvalde, Medina, Bexar, Comal and Hays counties, within the Nueces, San Antonio and Guadalupe river basins (Earl and Wood,

2002). Located within the San Antonio river basin is the Upper San Marcos River watershed (USMRW) (Fig. 2). The USMRW (61,035 acres) encompasses the drainage area for the Upper San Marcos River. However, for this study I assessed the drainage of one of its 6 sub-basins, the easternmost San Marcos sub-basin (SMSB). This nearly 11,000-acre area includes the city of San Marcos and contains the entire reach of the Upper San Marcos River. The river extends 7.5 km from its headwaters at Spring Lake Dam, fed from the underbelly of the Edwards Aquifer, down to its confluence with the Blanco River.

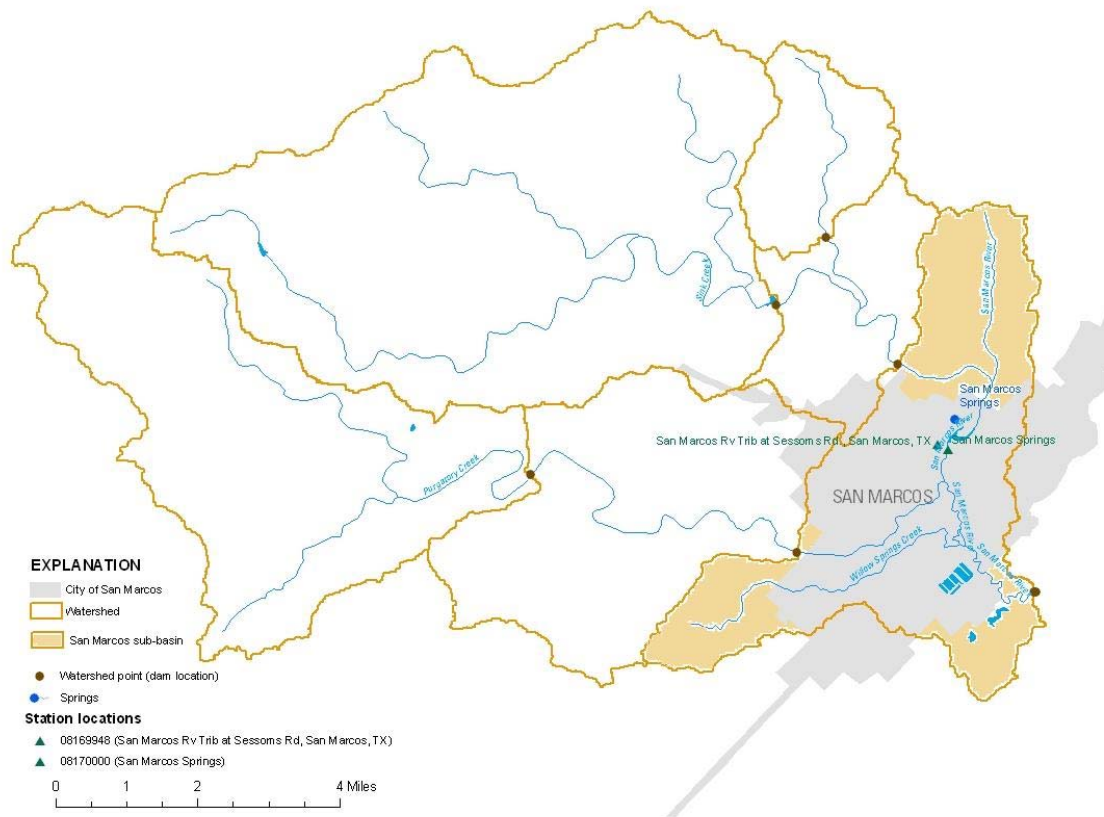


Fig. 2. Map of Upper San Marcos River Watershed, in Hays County, Texas. In tan is the San Marcos sub-basin (SMSB), which contains the Upper San Marcos River (USGS, 2007).

Nestled within the heart of a growing urban center, the river receives many disturbances. It is popular for recreational fishing, swimming, canoeing and tubing and has several street, railroad, and foot bridges that cross over it including Interstate 35 (Fig. 3). Furthermore, the river receives output from several culverts and tributaries, generally dry unless a rain event has occurred, as well as outflow from the Texas Parks and Wildlife A.E. Fish Hatchery and the City of San Marcos Wastewater Treatment Plant. The river is physically segmented by the placement of the Rio Vista and Cape's Dam, which help to regulate flow and create habitat (Saunders et al., 2001). Upstream of I-35 the riparian corridor is flanked by a greenbelt of public parks.

Spring Lake south half a mile downstream of I-35 is designated protected critical habitat (USFWS, 1995). Historically, the fountain darter was present in the entire river reach however the majority of recent individuals have been captured in Spring Lake and within the upper two-thirds of the river, generally upstream of the City of San Marcos Wastewater Treatment Plant (Saunders et al., 2001; Bio-West, 2006; T. Brandt, pers. comm., 2008; P. Connor, pers. comm., 2008). The individuals in the Upper San Marcos River (excluding the Spring Lake individuals) are those that make up the population under examination for this research.

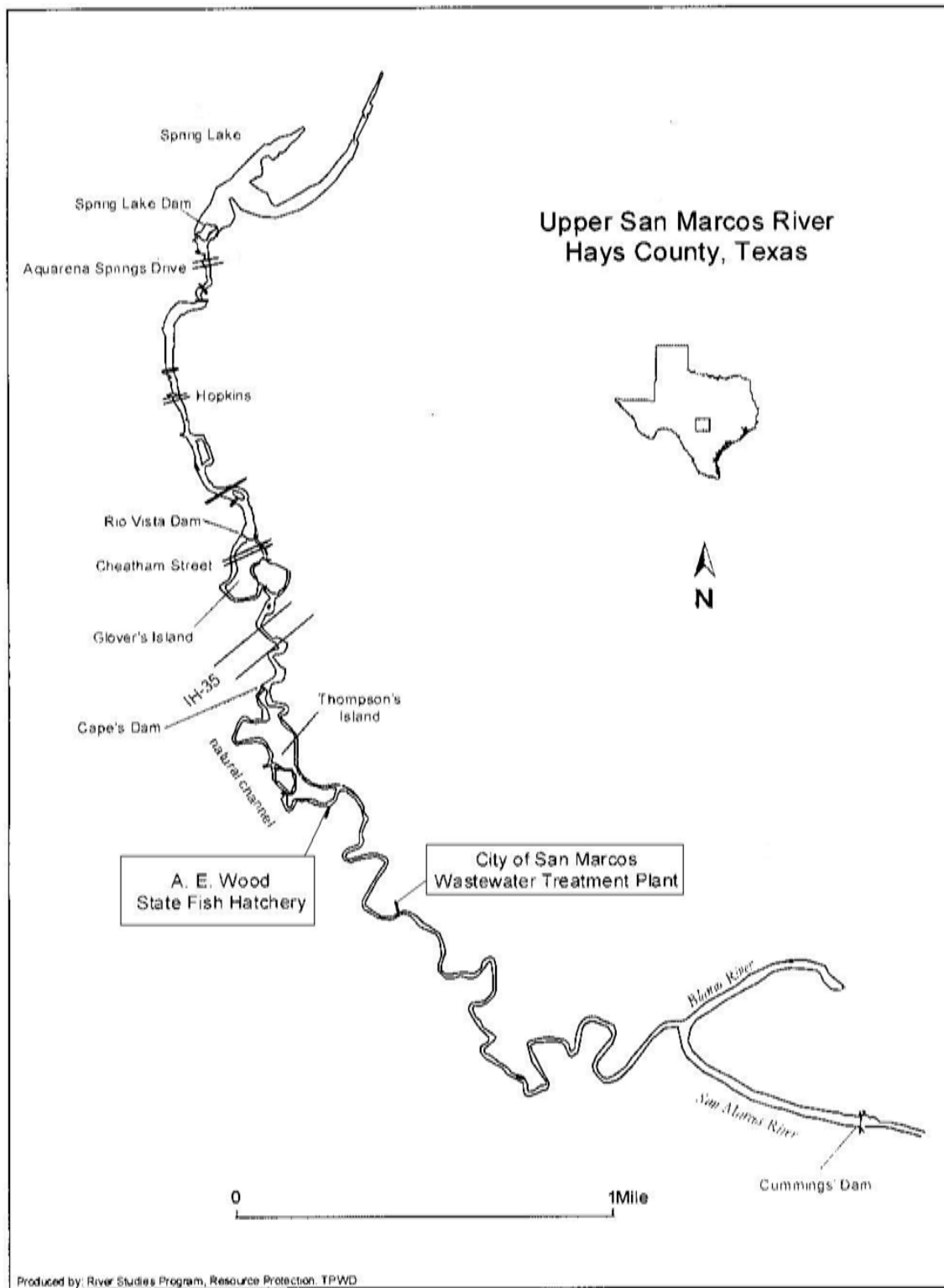


Fig. 3. Map of the Upper San Marcos River. Adopted from Saunders et al. (2001).

Conceptual model overview

Factors influencing the proliferation of a species are many and its interactions within an ecological community can be complex. Often research questions look to analyze a system at the landscape level or to test conditions of the future, which can be costly or physically impossible under the constraints of field assessments. Such is the case, especially concerning endangered species, where the future is of utmost concern, like in the Edwards Aquifer region. This is where simulation modeling is a valuable tool for ecologists.

As a platform for investigating integrated and complex systems, models assess the sensitivity of a system to its ecological factors and interactions. They are mathematical reconstructions that incorporate the ecological processes and parameters deemed valuable in solving a research problem. Ecologists are able to develop models, limited only by the knowledge about the system of interest, to test hypotheses, often times uncovering more questions in the process. I developed a population dynamics simulation model to determine how urbanization and its associated contaminants, driven by human population growth of the Edwards Aquifer region, will affect the survival and recovery of the endangered fountain darter in the Upper San Marcos River in Hays County, Texas into the year 2040.

The model simulates that heavy metal and organic contaminants enter and accumulate in the Upper San Marcos River. If specified concentration levels are ever reached, then darter mortality rates increase, thus affecting the total population over time. The eight contaminants of interest include 4 metals and 4 organics: cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), bifenthrin, carbaryl, dicamba and phenanthrene (PAHs).

The foundation of the model is a submodel of the darter population dynamics that is structured according to age (eggs, larvae, juveniles, adults) and sex (male and female). Six other submodels then represent survival pressures on the fish including: (1) San Marcos springflow; (2) watershed runoff; (3) contaminant concentration and (4) decay within the Upper San Marcos River; and fountain darter (5) ingestion and (6) excretion of PAHs.

The model simulates San Marcos sub-basin human population trends and impervious area to 2040. As impervious area increases, the levels of metals and PAH also increase but bifenthrin, carbaryl and dicamba levels decrease due to less pervious area. Rainfall events trigger runoff of contaminants to enter the Upper San Marcos River directly at 100, 50, or 30 percent of runoff. Once in the river, all contaminants but PAH accumulate or decay over time based upon their respective half-life. If the dissolved concentration ever exceeds the chronic (Cd, Cr, Cu, Zn) or acute (bifenthrin, carbaryl, dicamba) levels, then the darter population is subject to an increase in mortality rate. I modeled PAHs differently since they are hydrophobic and enter the river mostly bound to sediment. Rather than calculate the dissolved water concentration of PAH, the model determines the amount in fish tissue as a factor of gill and diet uptake and excretion rates. The model causes mortality at time t when the chronic tissue concentration has been exceeded. A summary of the model concept is diagrammed in Fig. 4.

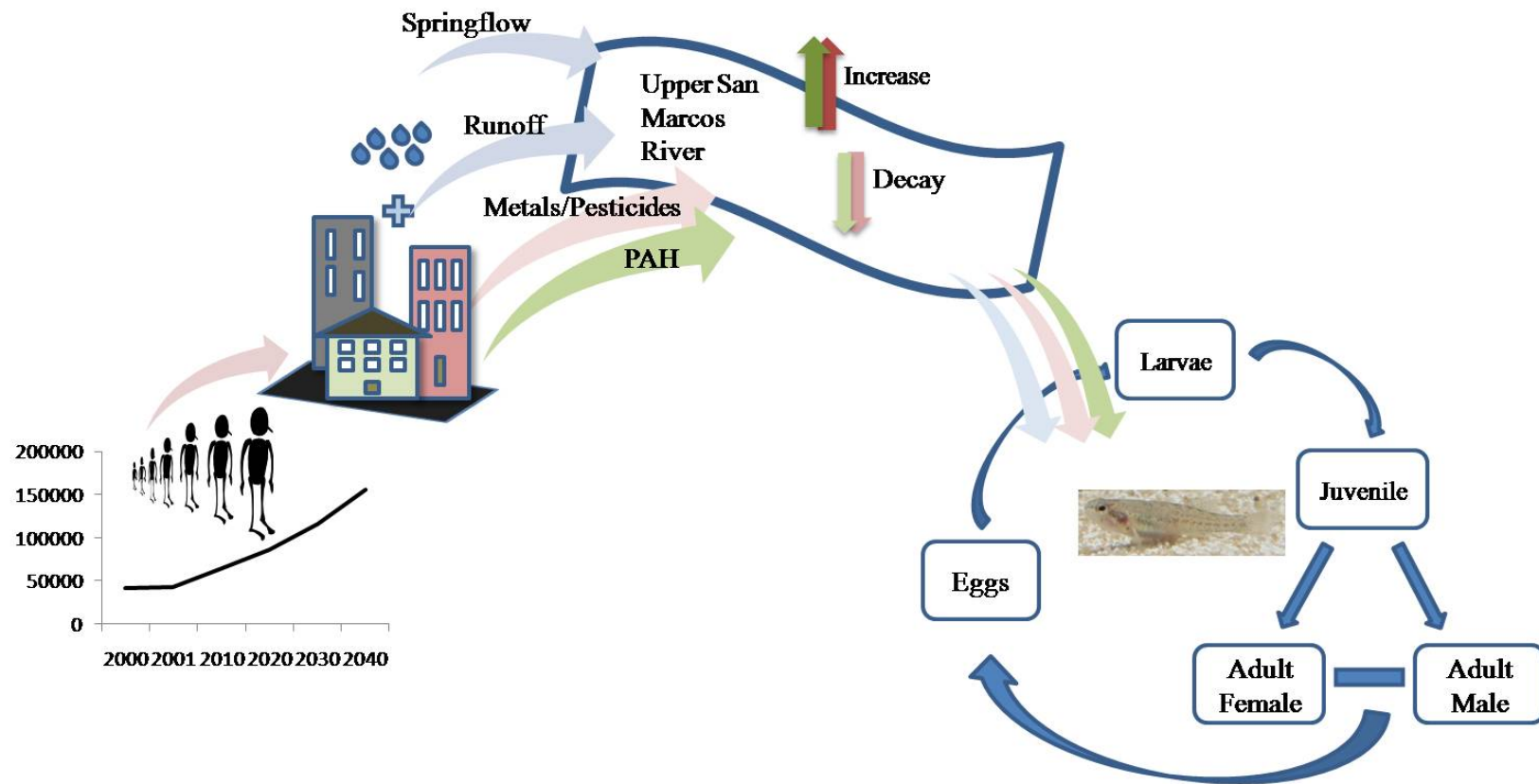


Fig. 4. Conceptual diagram of the modeled system-of-interest. This illustrates urbanization within the San Marcos sub-water basin, the non-point source pollution into the Upper San Marcos River and its impacts upon the fountain darters.

Description of model simulations

I assessed the fountain darter population under 10 different water quality treatments (Table 1). I individually simulated each contaminant to determine its possible impact on the darters (treatment 2–5 and 7–10). I also simulated the system with no contaminants (treatment 1) and with a combination of all metals (treatment 6) entering the river. Each treatment was subject to nine sets of simulation scenarios. A single simulation set models the system from 2008-2040 (n=50). Each scenario was a coupling of one of three springflow levels (random (R), high (H) and low (L)) with one of three runoff amounts entering the river (100, 50 and 30 percent) (Table 2). As an example, the modeled scenario of copper contamination simulated with high springflow and an expected 100 percent of runoff entering the river is Treatment 2, H-100. This nomenclature is followed throughout the document.

Table 1
Summary of text notation for modeled water quality treatments.

Treatment	Description
1	No changes to water quality
2	Copper
3	Zinc
4	Cadmium
5	Chromium
6	All metals (Cu, Zn, Cd, Cr)
7	PAH
8	Bifenthrin
9	Carbaryl
10	Dicamba

Table 2
Summary of text notation for simulated scenarios.

Scenarios	Description
R-100	Random springflow, 100 percent runoff
R-50	Random springflow, 50 percent runoff
R-30	Random springflow, 30 percent runoff
H-100	High springflow, 100 percent runoff
H-50	High springflow, 50 percent runoff
H-30	High springflow, 30 percent runoff
L-100	Low springflow, 100 percent runoff
L-50	Low springflow, 50 percent runoff
L-30	Low springflow, 30 percent runoff

Methods of simulation projection analysis

There were up to four parameters of interest for each simulation set: (1) the population trend over the simulated period (2008-2040), (2) the number of times per year that the concentration of a dissolved contaminant was projected to exceed the chronic aquatic life criterion, (3) the population on the last simulated day (December 31, 2040) and (4) the minimum population value over the simulated period. To determine the population trend over the simulated period I averaged the daily population values for the set ($n=50$) and then found the annual mean for years 2008 to 2040. Thus the population trend is the summary of simulated annual population means from 2008-2040 (\pm SE). The second parameter of interest was determined as an annual average of the number of times the concentration of a treatment chemical exceeded fountain darter thresholds.

Although prediction 3 and 4 can be inferred from the population trend, I wanted to test for statistical significance among the simulations and among the scenarios. To do so, I needed data values that were independent among samples. The trends in the first prediction are an average of all simulations and thus cannot be used for simple analysis of variance. However, values at a single time step within the model's projections are independent. Since this research is to determine what the survival and recovery of fountain darters might be into 2040, I choose the last simulated day and the minimum population values. To determine if the fountain darter population might be significantly lower under pressures of poor water quality versus good water quality and to test which contaminants cause the most significant decline, if any, I chose to analyze the last day value. Since the fountain darter is a species of concern, I chose to examine the statistical significance among the minimum population values, as it might be helpful in determining the minimum viable population number for sustainability of the fountain darters into the future.

I used the statistical program SPSS 11.5® for Windows® to run ANOVA *F* tests, Tukey's HSD tests and paired *t*-tests. I tested both the last day and minimum population values for difference among and between the scenarios with ANOVA *F* tests. To tease

out statistical significance among scenarios shown to be different, I used Tukey's HSD tests. The paired t-tests were used to determine if the population values under constraints of metals and organics in the water were significantly lower than the population values under clean water conditions. That is, scenarios R-100, R-50 and R-30 of each metal and organic treatments were compared to the corresponding population value (Scenario R) in clean water conditions; similarly scenarios H-100, 50 and 30 and L-100, 50, 30 were compared to Scenarios H and L, respectively, for clean water.

In summary, urban areas are hotspots of pollutants and modify the landscape surface, decreasing infiltration and increasing the chance of the pollutants to enter waterways by runoff. To determine how an aquatic endangered species might react to future urbanization and the associated potential toxic pollutants, I developed a computer simulation model. Within Chapter I, I identified the system-of-interest, provided background about the research problem, specified the study area, provided a conceptual overview of the model and identified the analytical procedures used to determine the survival trends, varied by future water quality conditions. The chapters that follow quantitatively explain the submodels involved to simulate and project survival in uncontaminated waters (Chapter II), water contaminated by metals (Chapter III) and water contaminated by organic chemicals (Chapter IV). I discuss all of the simulation results in Chapter V and conclude with Chapter VI.

CHAPTER II

IMPACT OF SPRINGFLOW VARIATION

Introduction

This chapter is the first of three that describe the fountain darter population dynamics model used to simulate population trends under different water quality conditions. Within this chapter, the fountain darter population is projected to 2040 under varying conditions of springflow. I assume that the Upper San Marcos River will remain uncontaminated into the future. I first provide background on the natural history of the fountain darter and its survival requirements. I then provide a quantitative description of the involved submodels. To develop a model properly, it must be evaluated for its ability to represent the system of interest and its interactions, which I describe before concluding with the simulation projections.

Fountain darter natural history

The fountain darters remain in only two locations in the world, the Comal and San Marcos Springs/River systems, both a result of the rechargeable Edwards Aquifer. Fountain darters require steady springflow, minimal water temperature variability, appropriate vegetation composition, and excellent water quality to survive. During the 1950s, a severe drought in the region led to Comal Springs ceasing to flow in 1956. This consequently led to extreme water temperature fluctuations and vegetation changes into the ecosystem, changes which the darters could not withstand. In 1975, no individuals were found in the Comal River/Spring system and darters from the San Marcos Spring population were introduced to repopulate (Schenck and Whiteside, 1976). Eighteen years after reintroduction the population in Comal was estimated to be 168,000 (Linam et al., 1993). Contrary to the Comal system the San Marcos springs has always flowed, its stability leading to unique habitat conditions that foster fountain darter survival (USFWS, 1995).

The USGS has collected daily springflow data since 1956 from water gauge number 08170500, located just below the Spring Lake Dam, at the headwaters of the

Upper San Marcos River and the daily average of flow (1956–2007) is 175 cfs. A no flow condition such as the 1950 drought highlighted the need to set up regulations regarding low flow condition. As dictated by the US Fish and Wildlife Service, springflow is of primary importance to the survival of the darters and should daily exceed 100 cfs in order to prevent take, jeopardy or adverse modification of critical habitat like the 1950 Comal event (USFWS, 1995).

The reason flow is so important is because its stability keeps the springs and river headwaters at a constant temperature, which is critical to early-life stage survival and reproduction of the fountain darter (Brandt et al., 1993; Bonner et al., 1998). At 23°C, eggs will hatch, on average, in 6 days with a hatch rate of 41 percent; the rate decreases when temperature is less than 20°C or more than 25°C (Bonner et al., 1998). Under extreme temperature fluctuations, the survival rates of eggs and larvae decrease (Schenck and Whiteside, 1977b; Simon et al., 1995). Once hatched, the fish are larvae for 2 months as they develop into juveniles (3-4 months) (Brandt et al., 1993; Simon et al., 1995). Living approximately 1-3 years, sexual maturity is reached between 3.5 months (Schenck and Whiteside, 1977b) and 6 months (Brandt et al., 1993). The constant temperature of the water enables year round spawning, which peaks in August and late winter (Schenck and Whiteside, 1977b; Hubbs, 1985).

Darters tend to remain in calm waters with currents of low velocity and in areas of dense vegetation (Linam et al., 1993). Similar to other species of darters, the population distribution is clumped; but unlike other species, fountain darters are not territorial (Strawn, 1956; Page, 1983). Darter densities positively correlate to filamentous algae coverage as it provides cover for adults and juveniles and is the substrate most often used for egg deposits during spawning (Strawn, 1956; Schenck and Whiteside, 1976; Linam et al., 1993). Should flow decrease, it would introduce sediment loads, water temperature variations and dissolved oxygen levels that can cause a redistribution or reduction of available habitat (Saunders et al., 2001). Therefore, as previously indicated, habitat quality and vegetation type, dependent on constant springflow, are critical to the survival and reproductive efforts of the darters. Thus, for

the first part of this assessment I wanted to simulate the population reaction to variation in springflow only, assuming that the water quality of the river will remain ideal (Fig. 5).

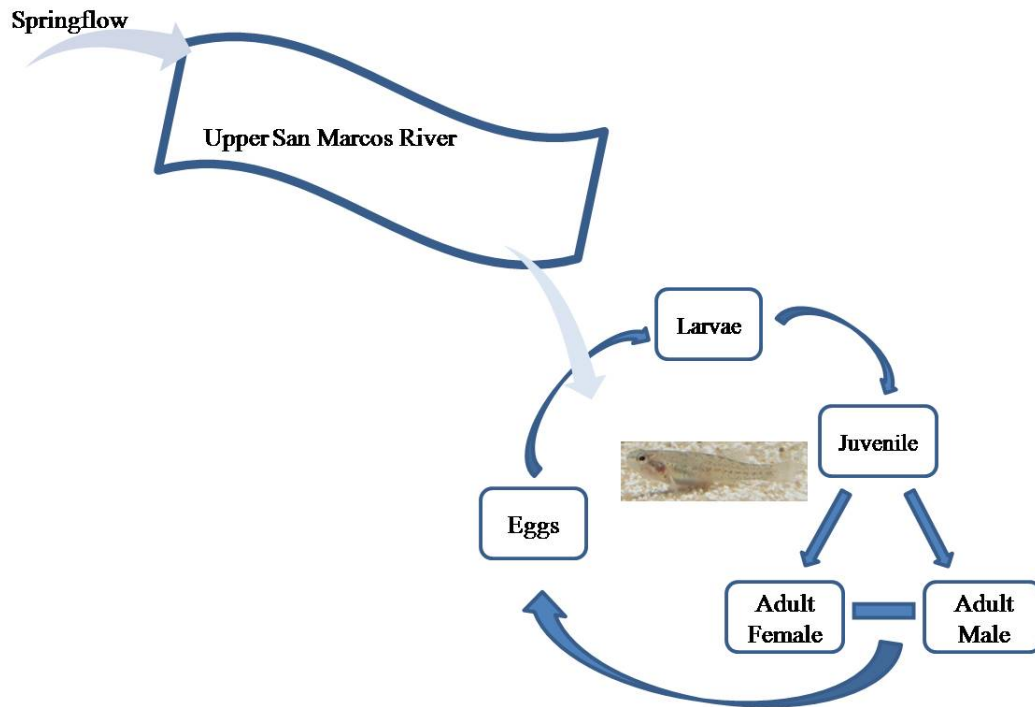


Fig. 5. Conceptual diagram of how the Upper San Marcos River springflow impacts the *E. fonticola* population.

Quantitative model description: *E. fonticola* dynamics & springflow

With STELLA® 7.0.1 Research for Windows®, I developed the Upper San Marcos River fountain darter population dynamics model using difference equations. It is a life stage and sex structured stochastic model which simulates 65 years (January 1, 1973 – December 31, 2040) using a daily time-step. State variables (rectangles) are factors of the system that accumulate over time, in this case fountain darters. The number of individuals within a state variable increases or decreases via material transfers, the arrows leading to or from rectangles. Individuals are recruited or leave the system via sources and sinks, respectively (clouds). A driving variable is any ecological

process that affects the system but is not affected by it (e.g. water temperature). The data or information within a driving variable is passed along to state variables via information transfers (thin arrows). These transfers indicate the state of the system during simulation and can alter the system. Any other information detailing the system of interest is programmed via constants and auxiliary variables (open circles).

Fountain darter population structure

Fountain darter life history is represented in Fig. 6 and is driven by recruitment and mortality. There are seven state variables representing number of eggs produced, larvae hatched, juveniles, males and females 6 months to 2 years, and males and females > 2 years to 3 years of age and 14 material transfers representing recruitment or survival and mortality at each life stage. The number of individuals within each state variable at time t (L_t) is calculated by the following equation:

$$L_{t+1} = L_t + (\Sigma_{\text{inflows}} - \Sigma_{\text{outflows}})\Delta t \quad (1)$$

where Σ_{inflows} is the total number of recruited individuals into life stage s and Σ_{outflows} is the total number of individuals leaving the state variable due to death or progression to the next life stage.

Within the model, eggs are produced (R) and accumulated in the state variable labeled E. There they develop for 6 days at which point they either hatch (SE) and develop into larvae (L) or fail to hatch and move out of the system (Em). As larvae, they are subject to mortality (Lm) or develop for 60 days to survive (SL) and become juveniles (J) for 120 days or die (Jm). At the point of maturity (6 months), the population is split into sexes based on a 1.39:1 sex ratio (SR, male (SJM) to female (SJF)). The first set of male and female state variables (F and M) accumulates adults over 550 days or eliminates them (Fm and Mm). If an individual survives to be 2 years (SF and SM), they then move into the second set of adult state variables (F2 and M2) which allows maturity to 3 years of age. Any individual that succeeds to be 3 years of age is eliminated from the system, no longer capable of producing offspring (F2m and M2m).

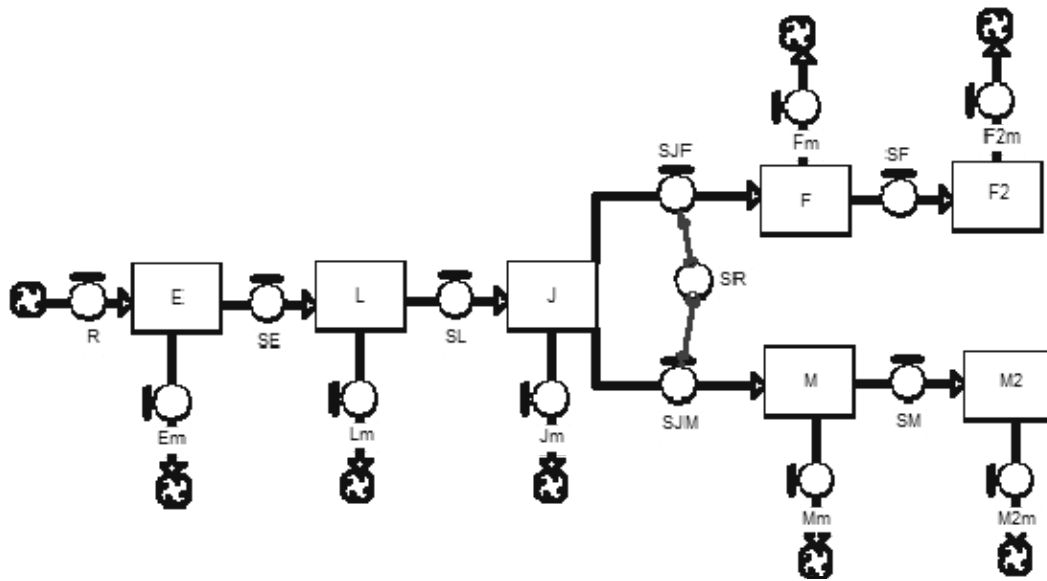


Fig. 6. Conceptual diagram of the fountain darter population dynamics model. Recruitment (R) and survival (SE, SL, SJF, SJM, SF, SM) are illustrated by arrows entering, and mortality (Em, Lm, Jm, Mm, Fm, M2m, F2m) is illustrated by arrows leaving. Squares represent state variables: number of eggs produced (E), larvae hatched (L), juveniles (J), males (M) and females (F) 6 months to 2 years and males (M2) and females (F2) 2 years to 3 years.

Recruitment

Base-level recruitment rates (R, production of eggs) are modified by the fecundity rate of the reproductively available females. Fountain darter females average 19 eggs per day (F_e) and although spawning occurs year round, there are peaks in reproductive activity (Schenck and Whiteside, 1977b). To calculate the number of reproductively available females at time t and account for seasonality, the total number of adult females at time t is multiplied by the daily percentage of ovulating females (Fig. 7) multiplied by fecundity. The number of eggs produced is then introduced into the system at the material transfer R (Fig. 6) and thus individuals are recruited into the population (E). In summary, number of eggs produced per day (R_t) is calculated by:

$$R_t = Mf_t * Tf_t * Fe \text{ where,} \quad (2)$$

$$Tf_t = F_t + F2_t \quad (3)$$

where Mf_t is percent of mature females actively spawning at time t (Fig. 7); Tf_t is the total number of mature females at time t as determined by adding the number of females 6 months to 2 years (F_t) and number of females > 2 years ($F2_t$) at time t and Fe is equal to eggs per females per day (19).

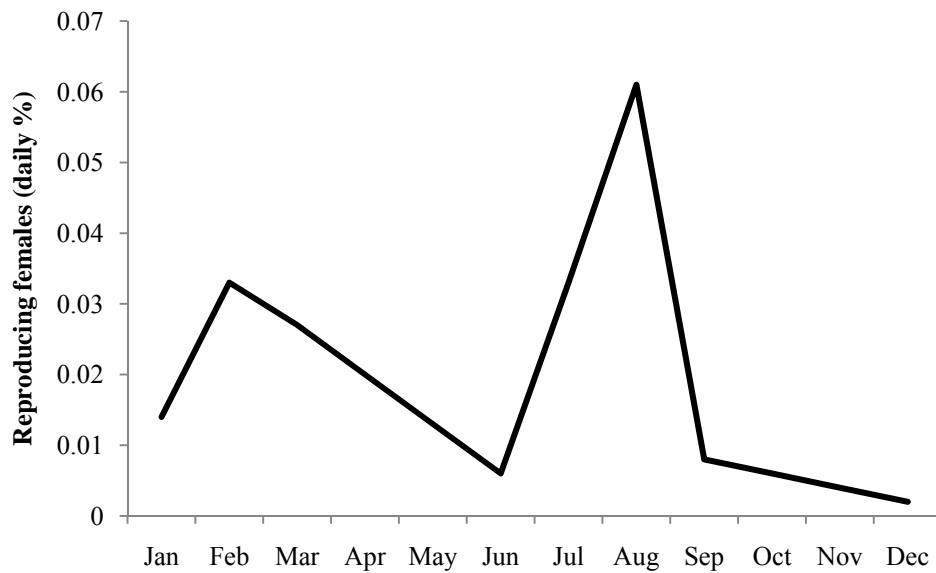


Fig. 7. Base-level seasonal variation for the daily percentage (varied by month) of simulated *E. fonticola* females that produce eggs. Adopted from graph of monthly percentages of females with mature ovum (Schenck and Whiteside, 1977b).

Mortality

The mortality rates in Fig. 6 (Em , Lm , Jm , Fm , Mm , $M2m$ and $F2m$) are a function of water temperature ($^{\circ}C$) and natural mortality rates as described in the following equations:

$$Em_t = emr_t + TE_t \quad (4)$$

$$Lm_t = lmr_t + TL_t \quad \text{where,} \quad (5)$$

$$TL_t = 1/(1 + e^{(-7.31 + 5.43 \cdot \ln(T))}) \quad \text{for temperatures (T) < 22°C else} \quad (6)$$

$$TL_t = 1/(1 + e^{(310.96 - 89.83 \cdot \ln(T))}) \quad \text{where,}$$

$$T_t = 20.74 + 0.228m_t + 0.031m_t^2 - 0.004m_t^3, \quad r^2 = 0.957 \quad \text{where,} \quad (7)$$

m = month (Jan = 1, Feb = 2, ..., Dec. = 12)

$$Jm_t, Fm_t, Mm_t = jamr_t \cdot TJA_t \quad (8)$$

$$F2m_t, M2m_t = a2mr_t \cdot TJA_t \quad (9)$$

where Em_t , Lm_t , Jm_t , Fm_t , Mm_t , $F2m_t$, and $M2m_t$ represent daily mortality rates at time t on eggs, larvae, juveniles, females and males 6 months to 2 years and females and males 2 to 3 years, respectively (Fig. 6). Rates emr_t , lmr_t , $jamr_t$, and $a2mr_t$ represent natural mortality rates at time t of eggs, larvae, juveniles, females and males 6 months to 2 years and females and males 2 to 3 years, respectively (Table 3). TE_t and TL_t are mortality rates due to temperature fluctuations for eggs (Fig. 8) and larvae at time t (Eq. 6), whereas TJA_t accounts for temperature fluctuations at the juvenile and adult stages at time t (Fig. 9). For equation 6, the river's water temperature (T_t) at time t is calculated by equation 7, developed from the average monthly water temperatures given in Saunders et al. (2001) under normal flow conditions (Fig. 10).

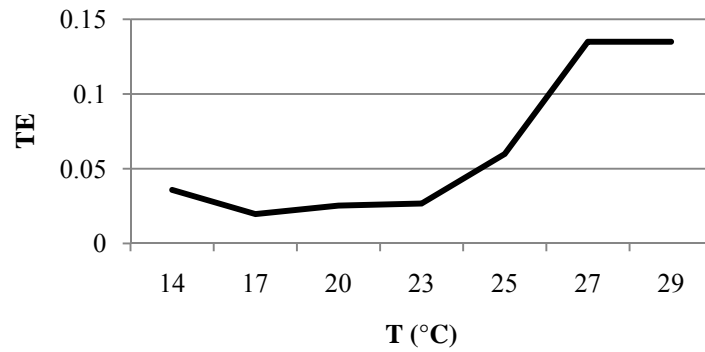


Fig. 8. Daily mortality rate of *E. fonticola* eggs at given temperatures. Adopted from Bonner et al. (1998).

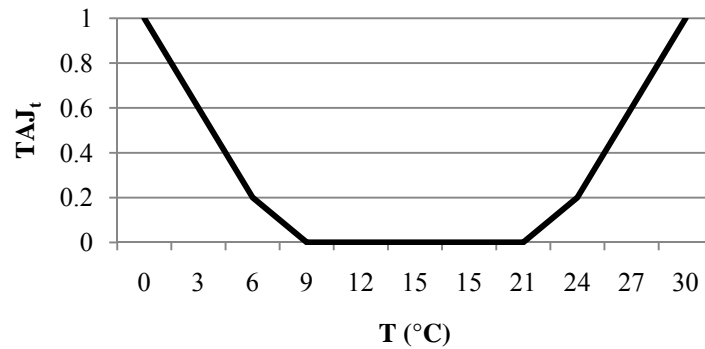


Fig. 9. Daily mortality rates of *E. fonticola* juveniles and adults at different water temperatures. Adopted from Bonner et al. (1998).

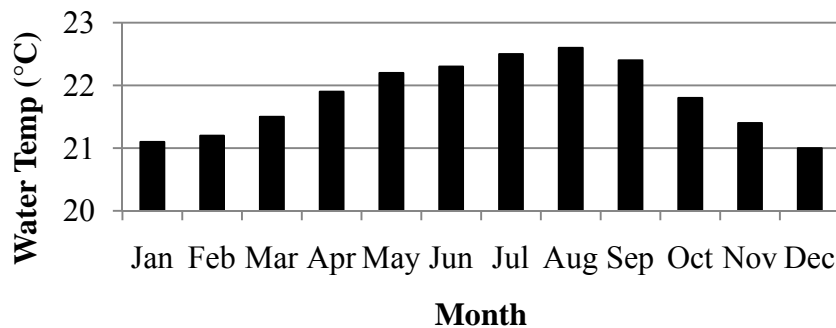


Fig. 10. Average monthly water temperatures for the Upper San Marcos River under normal flow conditions in 1995. Data used to develop equation 6 (Saunders et al., 2001).

Table 3
Base-level demographic fountain darter parameters for development, recruitment and mortality.

	Model Notation	Parameter	Value	Source
Development	E	Duration as egg	6 days	Simon et al., 1995
	L	Duration as larvae	60 days	Brandt et al., 1993
	J	Duration as juvenile	120 days	Brandt et al., 1993
	F, M	Duration as 6 m-2 y adult	550 days	Brandt et al., 1993
	F2, M2	Duration as 2-3 y adult	365 days	Brandt et al., 1993
	SR	Male to female sex ratio	1.39:1	Schenck and Whiteside, 1977b
Recruitment	Fcdty	Average mature ova/female/day	19	Schenck and Whiteside, 1977b
	Mf	Daily proportion of sexually mature females producing eggs	Fig. 7	Schenck and Whiteside, 1977b
Mortality	emr	Constant egg mortality rate	0.03	Pitcher and Hart, 1982; Brandt et al., 1993
	lmr	Constant larvae mortality rate	0.031	Pitcher and Hart 1982; Brandt et al., 1993
	jamr	Constant juvenile & adult mortality rate through 2y	0.00149	Brandt et al., 1993
	a2mr	Constant adult mortality rate > 2y	0.00545	Brandt et al., 1993
	TE	Egg mortality related to water temperature	Fig. 8	Bonner et al., 1998
	TL	Larvae mortality related to water temperature	Eq. 6	Bonner et al., 1998
	TJA	Juvenile and adult mortality related to water temperature	Fig. 9	Bonner et al., 1998
	T	Monthly average water temp (°C)	Eq. 7, Fig.10	Saunders et al., 2001

Springflow

The second submodel is springflow. Spring Lake discharge influences water quality and water quantity in the river downstream. Constant springflow can influence the vegetation, habitat and thus directly influence the life support system of the fountain darters. To simulate its impact on darters, I assumed that the population would react to a 30-day springflow average different from the average (175 cfs). I assumed that flow greater than 175 cfs is beneficial to the population whereas a flow less than 175 cfs

would cause a decline in numbers. This implies that when there is a lower than average springflow, fountain darter habitat conditions decline in the Upper San Marcos River. To calculate habitat decline on population, within the model, 175 is divided by the 30-day average of springflow at time t . If the value is < 1 then the population declines by a factor of 8×10^{-6} (determined through model development), if the value is ≥ 1 then the population remains stable or increases by that same factor. Decline of population occurs by increasing the mortality rate equally across all life stages and sex classes.

Since future springflows have not occurred, I assumed that future flows will be within the range of historical flows (Fig. 11). Therefore, daily future flows (2008-2040) are generated from daily historical flows as measured by the USGS gauge 08170500. For every future year the model simulates it randomly selects one year of past springflow (52 possible selections), whichever year (1956–2007) is selected, the model replicates.

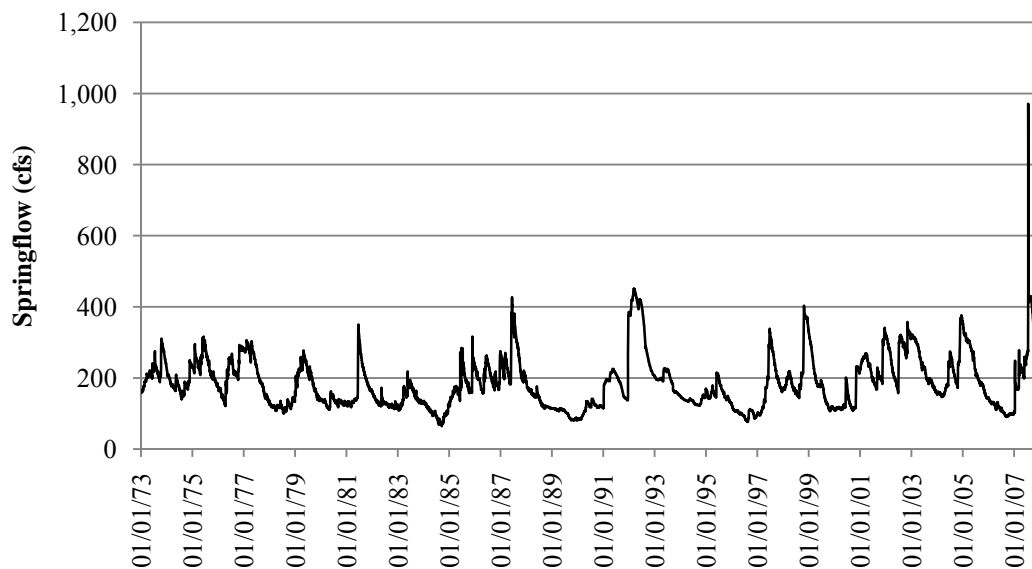


Fig. 11. Historical daily San Marcos River springflow (USGS gauge 08170500).

Model evaluation

I evaluated model performance by simulating the fountain darter population from 1973-2007 and compared the simulated values to population assessments from 1991 (Linam, 1993) and 2000-2007 qualitative data (Bio-West, 2007).

To test the model's predictions on population levels, I ran the model under historical conditions of human population, impervious area, and springflow. The model was initialized on January 1, 1973 with a population of 103,000 individuals (Schenck and Whiteside, 1976). Those individuals were split among the life stage state variables according to the proportion estimates for January from the long-term study of Bio-West, Inc. (2007). Therefore, 77 percent of the 103,000 individuals were sorted into adults according to sex ratio and 23 percent were placed as juveniles. The initial human population and total impervious area percentage of the sub-basin were 19,145 and 34, respectively (USGS, 2007). Daily springflow values in the model were those of the historical daily springflow values as measured by the USGS water gauge 08170500 for the period of 1973-2007 (Fig. 11).

Simulated historical trends compare favorably with available information on *E. fonticola* population estimates. Schenck and Whiteside (1976) performed an assessment in 1973, estimating a population of 102,966 individuals. Although the model was initialized at 103,000, it predicted that the average annual population for 1973 was 101,178, a 1.74 percent difference from the Schenck and Whiteside estimate. In 1991, another assessment of the population was made by Linam (1993), estimating the population to be 45,900 with a range of -15,900 to 107,700 (90% CI). The model predicted that the average 1991 population was 45,312, well within the 90% confidence interval, only a difference of 1.28 percent.

Furthermore, simulated populations were relatively stable over the period from 1985-2007 (Fig. 12), which compares favorably with results of an 8-year field study which also reported stable population from 2000-2007 (Bio-West, 2007). The model predicted that the population mean from 2000-2007 was $64,062 \pm 11,424$ individuals (mean \pm SD), further suggesting stability (Fig. 13). Lastly, qualitatively, a biologist

intimately associated with the San Marcos River, went on record that he recognized a decline in population between 1975–1995 (USFWS, 1995). The simulated results do show a decreasing trend for that time period (Fig. 12).

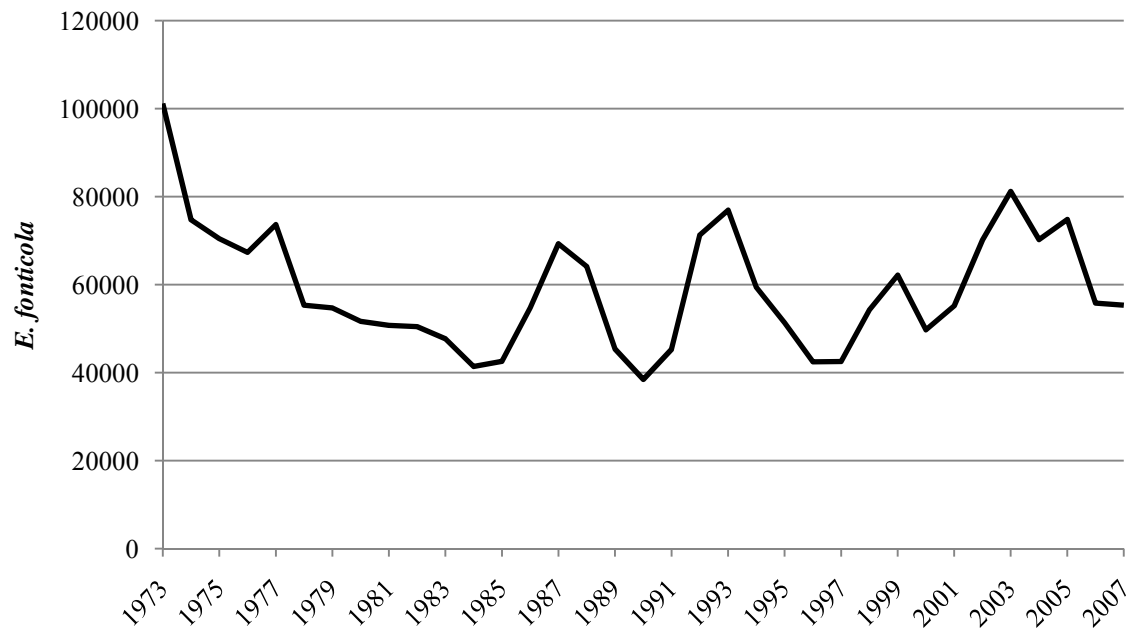


Fig. 12. Simulation results of mean annual *E. fonticola* population in the Upper San Marcos River from 1973 to 2007.

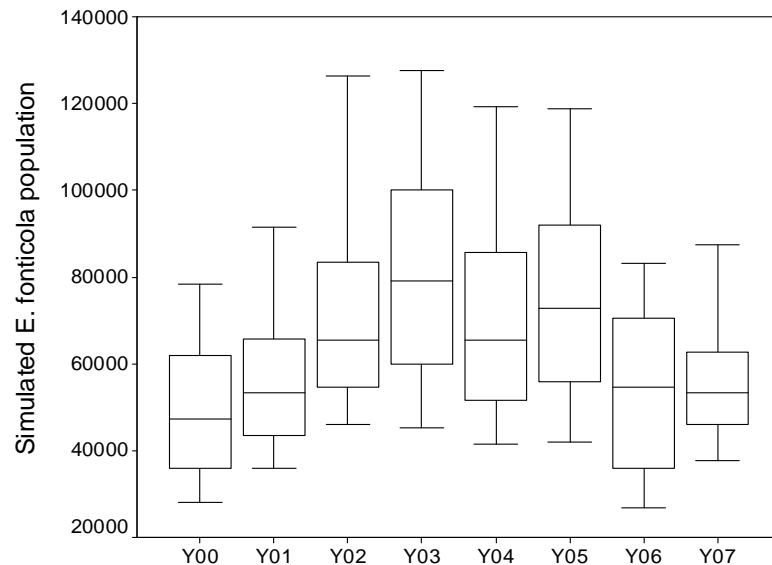


Fig. 13. Variance of simulated annual *E. fonticola* during the period 2000-2007.

Not only did I evaluate the model for its ability to replicate historical population values but I evaluated its capacity to simulate life stage classes. I compared simulated life stage distributions to those of a field study in 2005 (Bio-West, 2006). For the 2005 sampling season, 11% of darters captured in drop nets in the San Marcos River were larvae (6-15mm), 28% were juveniles (16-23 mm) and 61% were adults (>23 mm) (Bio-West, 2006). As for my model, in 2005, larvae made up an average of 46% of the population, whereas 15% were juveniles and 39% were adults. Although simulated and capture proportions were not exactly the same, results show that there are more juveniles than adults, both under natural and simulated conditions. This is an attribute of a healthy fish assemblage. As the field assessment did capture some larvae, it shows that there is some reproduction occurring year round and was simulated as such in the model. It must be taken into consideration that drop nets in the field might have a bias for large size class individuals (juveniles and adults) and that sampling was done on a seasonal basis.

Simulation of springflow variation on *E. fonticola*

After model development and evaluation, I then simulated springflow variation and assessed its impact on the darters. I ran simulations ($n=50$) of three future (2008–2040) scenarios (R, H, and L). In scenario R, springflow for every future year simulated is a replicate of the daily springflow values from a historical year (1956–2007) selected at random. Scenario H simulates future flows as in scenario 1 except for future years 2010, 2020, 2030, and 2040. These are designated as high flow years (annual mean >190 cfs) and are random replicates of 1987, 1991, 1992, 1998, and 2007. Scenario L replicates all years at random except for 2009–2010, 2019–2020, 2029–2030, and 2039–2040. These are designated as low flow years (annual mean <108 cfs) and are random replicates of 1956, 1963, 1964, 1967, 1984, and 1996. There were three predictions of interest: (1) the population trend over the simulated period (2008–2040), (2) the population value on the last simulated day (December 31, 2040) and (3) the minimum population value over the entire simulated period.

Simulated population trends

The mean population of *E. fonticola* over the simulated period (2008–2040, $n=32$) for scenario R (54155 ± 2926 (mean ± 2 SE)) was less than that of scenario H (57264 ± 3139) but greater than scenario L (48428 ± 2344). Results show that with a 95% CI, the model predicted the annual mean population for fountain darters from 2008–2040 to range from 46,084 to 60,403 individuals. For scenario R at all years, except for 2008 and 2009, the population remains stable around 54,000 individuals whereas in scenario H and L there are respective increases or declines at years that were designated high or low (Fig. 14).

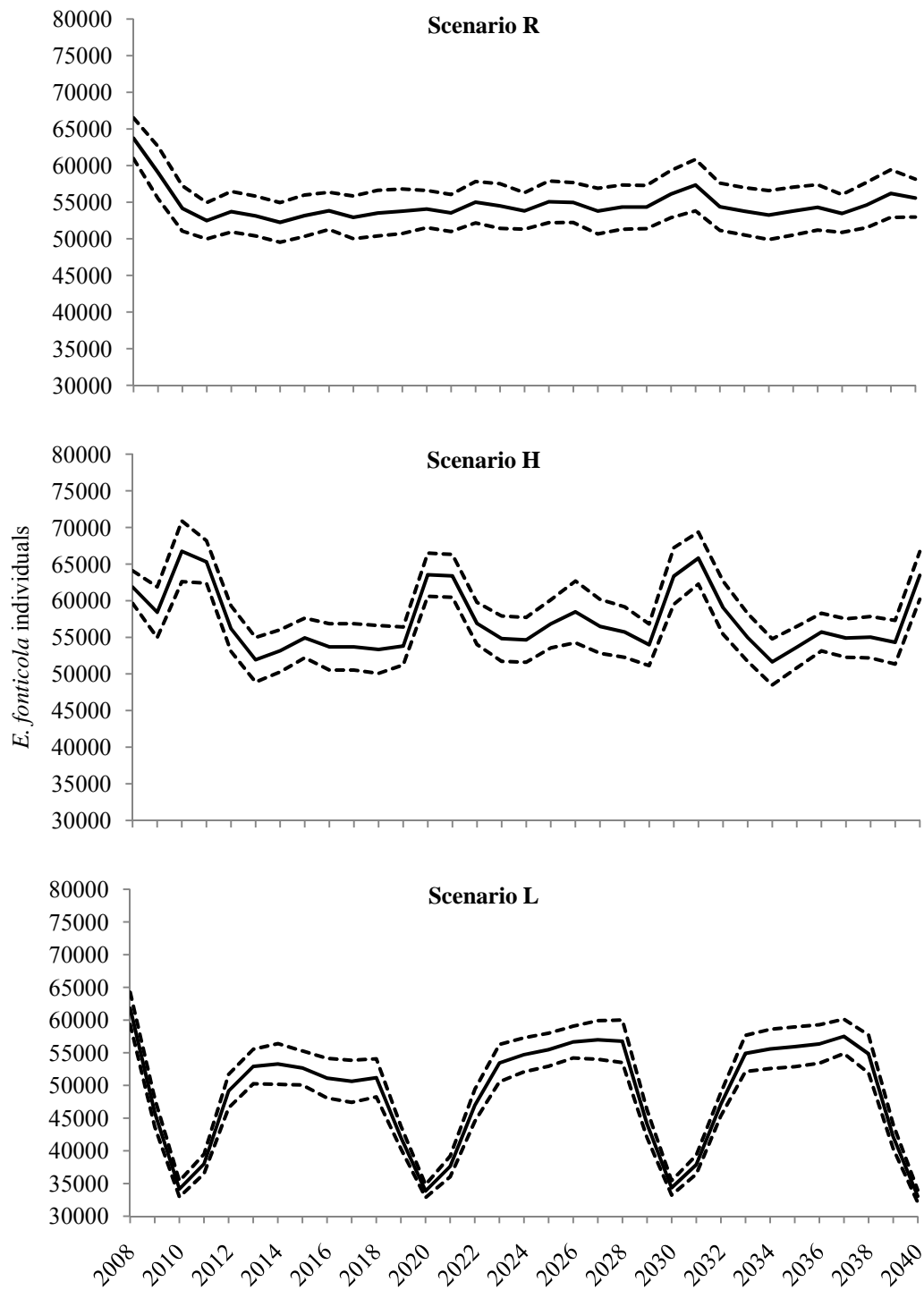


Fig. 14. Annual mean population of *E. fonticola* under random (R), high (H) and low flow (L) simulation ($n=50$) scenarios of uncontaminated water. Dotted lines represent ± 2 SE.

Simulated last day and minimum population values

Besides the population trend, I was interested in determining if the populations by the end of the simulation (December 31, 2040) and the minimum were different among scenarios R, H and L (Table 4). I used ANOVA F tests in SPSS 11® for Windows® to determine that between scenarios, the mean last day ($F=228$, $p < 0.001$, $df=149$) and mean minimum values ($F=29$, $p < 0.001$, $df=149$) were significantly different.

To tease out significance, I then analyzed the data with Tukey's Honestly Significant Difference tests. For the last day means, all three scenarios were significantly different from one another. The population under high flow was significantly greater than the population at random flow which was greater than the population at low flow conditions. As for the minimum values, mean at low flow was significantly lower than both the mean at random and high flow conditions.

Table 4

Summary of simulated mean *E. fonticola* population values on December 31, 2040 and the mean lowest daily population over the simulated period (2008–2040) under conditions of clean water.

Scenario ^a	December 31, 2040		Simulated minimum	
	Mean (SD)	95% CI	Mean (SD)	95% CI
R	33170 (5977)	31472–34869	19509 (2772)	18736–20283
H	41926 (7079)	39914–43938	19037 (3182)	18132–19941
L	18729 (2153)	18117–19340	15790 (1845)	15266–16315

^a n=50

CHAPTER III

IMPACT OF HEAVY METAL TOXICITY

Introduction

As the second of a three part series, this chapter builds upon the fountain darter population structure and springflow submodels in the previous chapter to examine urbanization impacts, as indicated by metal toxicity, on the fountain darters to 2040. I begin with a brief introduction to heavy metal toxicity in aquatic environments. This is followed by the quantitative description of an additional three submodels that represent runoff and metal concentration for the modeled river. I end the chapter with a summary of the simulation results.

Background: Cu, Zn, Cd, Cr

When it rains, the nature of water is to infiltrate or percolate into the soil, taking with it any metal ions that might have been on the surface. Once in the soil, the metal ions will adhere to the particles, thus soil acts as a purification system for our waterways. However, as an area urbanizes the landscape often eliminates pervious surfaces increasing runoff, decreasing purification. To compound the problem, urban areas often are hotspots of pollution. Thus, a decrease in pervious area will enhance the concentrations of contaminants such as heavy metals, pesticides, insecticides and hydrocarbons in storm runoff and ultimately in surface waters (Wheeler et al., 2005). Within the waters, the particles will accumulate if persistent, and can concentrate up in the aquatic food chain. This is of particular concern for endangered species because toxicity can ultimately led to mortality and a reduction in population. Thus, I wanted to model heavy metal toxicity and its impact on fountain darters should the city of San Marcos continue to grow as projected.

Any number of metals can be present in the environment and influence the health of the ecosystem. I selected four to model and represent heavy metal toxicity impacts on the fountain darters: (1) zinc, (2) copper, (3) chromium and (4) cadmium. These four metals met the following requirements. They are all considered priority pollutants by

the US EPA (2006). Secondly, there is substantial documentation of their presence and accumulation within urban streams and rivers. Thirdly, the majority of their environmental deposition beyond natural levels comes from anthropogenic sources. Lastly, they all are potentially toxic for aquatic organisms, specifically the fountain darter.

Many studies have assessed the chemical composition of urban and road runoff (Muschack, 1990; Wu et al., 1998; Davis et al., 2001; Brezonik and Stadelmann, 2002; Kim et al., 2005). As indicated before, the most common metals in urban streams include zinc, copper, cadmium, lead, chromium, and nickel (Muschack, 1990; Paul and Meyer, 2001). Those with the highest runoff concentrations are: zinc (20–5000 µg/L), copper (5–200 µg/L), chromium (<24 µg/L) and cadmium (<12 µg/L) (Muschack, 1990; Davis et al., 2001). These metals occur within the Edwards Aquifer but at low concentrations but this can change as the landscape includes more urban development. As of 2005, within the Edwards Aquifer the typical ranges were not detectable (ND)–20 µg/L (zinc), ND–4 µg/L (copper), ND–3 µg/L (chromium) and ND–0.6 µg/L (cadmium) (EAA, 2006a).

Metal concentrations beyond the natural background sources come from a variety of anthropogenic causes. The particles can be byproducts of combustion processes (e.g. oil, wood or coal), mining, pesticide/herbicide use and are used in wood preservatives, electronics, home improvement materials (e.g. paint), or even batteries (Newman and Unger, 2003). However, hotspots in urban areas subject to runoff include residential and commercial buildings (Steuer et al., 1997; CWP, 2003). In fact, 31 percent of copper, 65 percent of zinc, and 26 percent of cadmium within runoff is from building siding and roof particles (Davis et al., 2001). The second most significant impervious areas within a city include paved areas, such as parking lots and streets (CWP, 2003; TDCE, 2004). Wear from vehicle brake linings account for 47 percent of the copper in runoff and tire wear accounts for 27 percent of the zinc and 10 percent of cadmium in runoff (Davis et al., 2001). Thus, simply two urban components (buildings and vehicle wear on roadways) can account for 78, 93 and 36 percent of the dissolved copper, zinc and

cadmium, respectively, in runoff. Therefore, as an area urbanizes, the pervious area declines, pollution sources increase and the potential for aquatic toxicity to occur due to water chemistry changes increases.

To have concentrations greater than natural background levels is a concern for aquatic life, especially endangered species like the fountain darter, because it can cause direct mortality or have sublethal affects that can reduce survival. Toxicity is often assessed at two levels: acute or chronic. For the model, I assess chronic mortality, as this would show the greatest impact on the population over time. The most toxic of the four metals is cadmium ($EC_{10} = 0.89 \mu\text{g/L}$ (53 d)), followed by copper ($IC_{10} = 8.1 \mu\text{g/L}$ (60 d)), zinc ($EC_{10} = 88 \mu\text{g/L}$ (69 d)) and chromium ($IC_{20} = 340 \mu\text{g/L}$ (30 d)) (Benoit, 1976; Besser et al., 2001; Mebane et al., 2008).

Of the metals, only copper toxicity has been directly tested on fountain darters therefore I needed to use a surrogate species to quantify toxicity responses for the other three metals. The US EPA tested surrogated species and found that the darters were more sensitive than the fathead minnows but were not more or less sensitive than rainbow trout (Besser et al. 2005; Dwyer et al., 2005). White et al. (2006) discuss water quality recommendations for the fountain darter and conclude that early-stage rainbow trout should be the surrogate species modeled when darter reactions to water quality changes are unknown. Furthermore, depending upon the metal, toxicity can vary among life stages however generally larvae or post-hatched individuals are the most susceptible (Mance, 1987). I therefore used larvae toxicity tests for fountain darters when available (copper) and use larvae/post-hatched rainbow trout as the surrogate species for toxicity results for cadmium, zinc and chromium.

To summarize, as the San Marcos sub-basin becomes more impenetrable to water, greater quantities of runoff will flow over the landscape, into the spring and river rather than seep into the ground and be naturally purified by the soil. Such direct contamination to the river can potentially decrease water quality, destroy habitat and food sources that the fountain darter relies upon. Chemicals that slowly degrade and persist in the environment like heavy metals are of particular concern and so I modeled

copper, cadmium, chromium and zinc discharges into the San Marcos River and their subsequent impacts upon the darters into 2040 (Fig. 15).

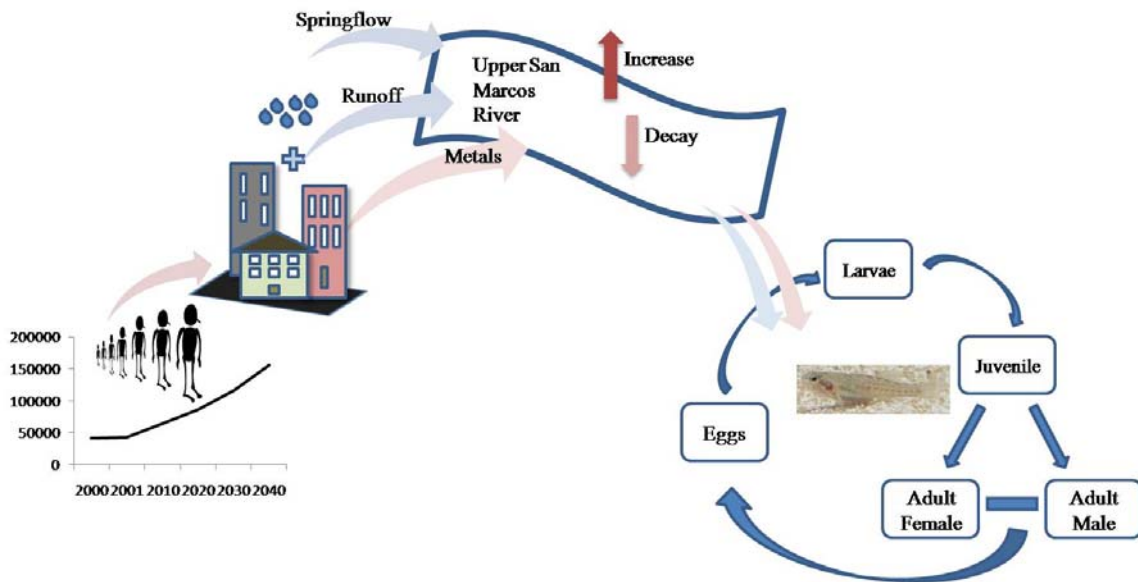


Fig. 15. Conceptual model of how metals enter the Upper San Marcos River and its impact upon the fountain darter population.

Quantitative model description: metals

The three subsequent submodels (runoff, contaminant concentration and contaminant decay) were developed and incorporated into the population dynamics model of Chapter II to predict heavy metal impacts on fountain darters.

Runoff

The runoff submodel calculates the annual runoff (acre-inches) of the San Marcos sub-basin as a factor of percentage of total impervious area (acres) and annual precipitation (inches). Runoff can be determined several ways, I used the “Simple Method” developed by Schueler (1987) which calculates annual runoff as well as contaminant concentration from percentage of total impervious area and select information about a watershed. The model calculates the annual runoff in acre-inches

per year (Q) from the following equations:

$$Q_t = 0.9 * R_{c_t} * A * P_t \quad \text{where,} \quad (10)$$

$$R_{c_t} = 0.05 + 0.9(TIA_t), \quad r^2 = 0.71 \quad \text{where,} \quad (11)$$

$$TIA_t = 23.6 + 0.000565185 * G_t \quad (12)$$

where 0.9 represents the fraction of annual rainfall events which produce runoff (CWP, 2003); R_{c_t} represents a runoff coefficient that corresponds to the percentage of impervious area at time t ; A is the area of the sub-basin (10,670 acres); P_t equals the annual rainfall depth in inches at time t and TIA_t equals the percentage of total impervious area as a function of human population (G_t). Future P_t is simulated via random selection of annual rainfall values for 1973-2007 (Fig. 16) and human projections are equal to the values in Fig. 17.

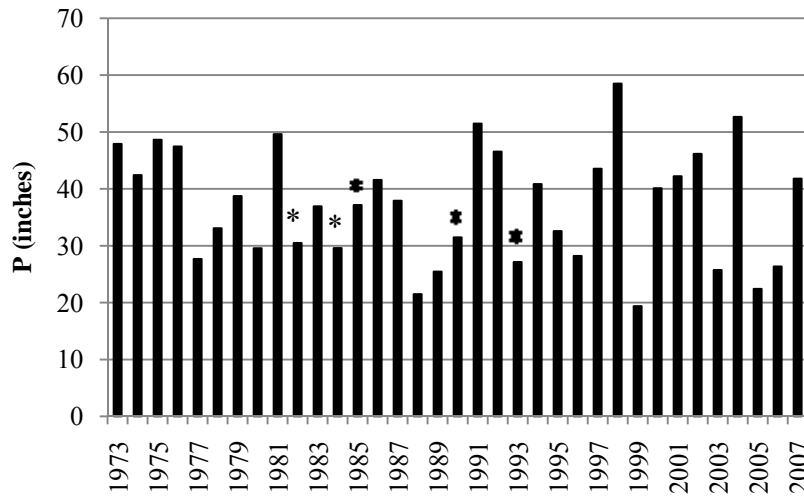


Fig. 16. Annual precipitation (inches) for city of San Marcos (1973–2007) (NOAA, * Austin; NOAA, San Marcos).

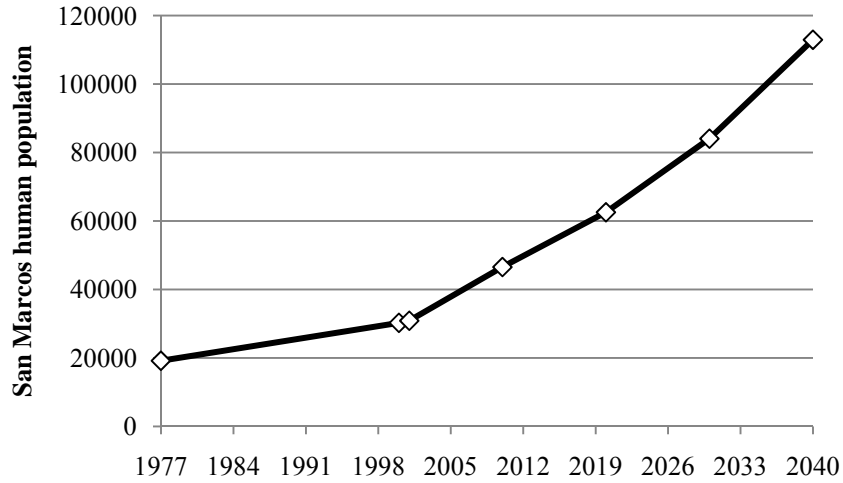


Fig. 17. Human population of San Marcos, Texas as projected by USGS (2007).

Contaminant concentration

The contaminant load submodel determines the dissolved concentration of a metal in the Upper San Marcos River as a factor of its annual mass (lbs), converted into a daily mass (μg) and then dissolved in the daily springflow volume (cfs).

Annual contaminant mass

I continued to use the “Simple Method” (Schueler, 1987) to estimate future annual contaminant loads (ACL).

$$ACL_t = Q_t * EMC_c * 0.226 \quad (13)$$

where Q_t is annual runoff in acre-inches; EMC_c is the estimated mean concentration of chemical c (Zn, Cr, Cd, or Cu) per rain event in mg/L (Appendix B) and 0.226 converts ACL into pounds.

Daily contaminant mass

The model transforms ACL from annual mass to daily mass as a factor of rain events. Any time it rains, ACL is multiplied by the daily proportion of rainfall at time t (P_t). To simulate daily rainfall for a future year, the model randomly selects from 8

historical years (2000–2007) of daily rainfall patterns. Therefore, in the model, the annual load of contaminant c , at time t , is multiplied by the daily proportion that corresponds to one of eight daily rainfall variations. So on days that it does not rain, no contamination enters the system but on days it does rain it is according to the daily fraction of annual rainfall for the simulated year. The daily contaminant load (DCL) is calculated by the following equation:

$$DCL_t = ACL_t * dp_t * ug_t * cf \quad (14)$$

where ACL_t is the annual contaminant load in pounds; dp_t is the daily proportion of rainfall at time t ; ug converts from pounds to μg (equal to 453592370); and cf is a fraction of the load that makes it into the river (equal to 1, 0.5, or 0.3).

Load concentration

To be able to simulate impacts of heavy metals on fountain darters, I needed to transform the daily mass to a daily concentration in the river. The volume of water in the San Marcos River (SMv) is a factor of flow which accounts for runoff quantity:

$$SMv_t = [(8566.85 * sf_t) + 3149450] * 28.317 \quad (15)$$

where sf_t is equal to springflow (cfs) at time t and 28.317 converts cfs to liters. Thus, to determine the dissolved concentration ($\mu g/L$) of a contaminant in the Upper San Marcos ($SMCc$) at time t , DCL_t is divided by SMv_t . The relationship between springflow and volume of river water was determined from the data in Saunders et al. (2001).

Contaminant decay

The third metal submodel estimates the quantity of a contaminant as it increases or decays over time within the river and calculates when levels exceed fountain darter life criterion, triggering mortality at the larval stage.

Daily dissolved concentrations ($\mu g/L$) of zinc, cadmium, chromium and copper, are factors of the concentration within the river ($SMCc$), their respective decay rate as

determined by half-life in water (Cl) and background levels with the river. The average concentration of a metal (Ca_c) is taken over a designated time associated with a chronic level threshold. For every time Ca is greater than the set threshold, an associated mortality rate (Cm) is added to the rate already determined for time t (Chapter II). Larvae are the most susceptible life stage for most fresh water fish and hence are the individuals within the model affected by Cm . The model parameters for all metals are summarized in Table 5.

To summarize, the former three submodels determine the quantity of a metal entering the river, its accumulation and decay, and stimulates a larval mortality event should a chronic concentration level be reached. For example, if the 30-day average concentration of copper ever exceeds 8.1 $\mu\text{g/L}$ then it will result in a ten percent decline added to the mortality rate for larvae at time t .

Table 5
Base-level half lives and chronic toxicity levels for metal parameters.

Metal	Model Notation	Value	Source
Cadmium	Cl ^a	15 days (0.045)	Baccini et al., 1979
	Ca ^b	0.89 $\mu\text{g/L}$ per 53 days ^d	Mebane et al., 2008
	Cm ^c	0.1 if 0.89-1.2 $\mu\text{g/L}$, 0.2 if >1.2 $\mu\text{g/L}$ ^d	Mebane et al., 2008
Chromium	Cl	28 days (0.0244)	Cranston and Murray, 1980
	Ca	340 $\mu\text{g/L}$ per 30 days ^e	Benoit, 1976
	Cm	0.2 ^e	Benoit, 1976
Copper	Cl	10 days (0.0669)	Effler et al., 1980; Adams et al., 2000
	Ca	8.1 $\mu\text{g/L}$ per 30 days ^f	Besser et al., 2001
	Cm	0.1 ^f	Besser et al., 2005
Zinc	Cl	25 days (0.0273)	Adams et al., 2000
	Ca	88 $\mu\text{g/L}$ per 69 days ^g	Mebane et al., 2008
	Cm	0.1 if 88-147 $\mu\text{g/L}$, 0.2 if >147 $\mu\text{g/L}$ ^g	Mebane et al., 2008

^a Half-life dissolved in water

^b Average chronic contamination level not to be exceeded

^c Mortality rate if chronic contamination level is exceeded

^d EC₁₀ for early-life stage rainbow trout, 53 d duration

^e IC₂₀ for early-life stage rainbow trout, 30 d duration

^f IC₁₀ for early-life stage fountain darter chronic toxicity test

^g EC₁₀ for early-life stage rainbow trout, 69 d duration

Simulation of metal toxicity on *E. fonticola*

To predict future heavy metal impacts on the San Marcos system, I simulated five treatments of water quality conditions. Water was contaminated by one metal (Cu, Cd, Zn, Cr) at a time (treatments 2–5) or by all metals (treatment 6) to determine the additive affect. The model simulated each treatment nine times; each a different combination of springflow and percent runoff entering the river (R–100, 50 or 30; H–100, 50 or 30; and L–100, 50, or 30). There were four predictions of interest: (1) the population trend over the simulation period (2008–2040), (2) average number of times dissolved metal concentrations exceeded the chronic aquatic life criterion for each simulated year (mortality events), (3) the population value on the last simulated day (December 31, 2040) and (4) the minimum population value over the entire simulated period.

Simulated population trends

In general, the modeled population declined the most when all metals entered the system (Figs. 18–20) regardless of springflow or runoff scenario. Individually and regardless of springflow/runoff conditions, copper caused the greatest decline, followed by zinc and then cadmium (Figs. 21–29). Chromium caused no decline in population. At 100% runoff and with all metals, the population fell below 23,000 (half of the most recent estimate of ~46,000, Linam (1993)) by 2024 under random flow, by 2026 with forced high flows and by 2020 with forced low flow conditions (Table 6).

Table 6
Influenced by metal toxicity, the mean 2040 populations and the average year that the population decreased by 50% of the most recent field estimate.

Scenario	Metals		Cu		Zn		Cd		Cr	
	2040	Year	2040	Year	2040	Year	2040	Year	2040	Year
R –100	2164	2024	5887	2028	11230	2032	47280	–	54844	–
R– 50	29286	–	30094	–	41667	–	55677	–	56185	–
R – 30	43792	–	42880	–	54653	–	55436	–	55189	–
H – 100	2565	2026	7152	2027	11835	2033	55199	–	60417	–
H– 50	36941	–	30837	–	45262	–	64080	–	66060	–
H–30	51561	–	48370	–	60150	–	62637	–	61571	–
L–100	1390	2020	4550	2028	7108	2030	27931	–	33196	–
L–50	16959	2040	18718	–	24419	–	33750	–	34056	–
L–30	26722	–	27305	–	31941	–	34135	–	33540	–

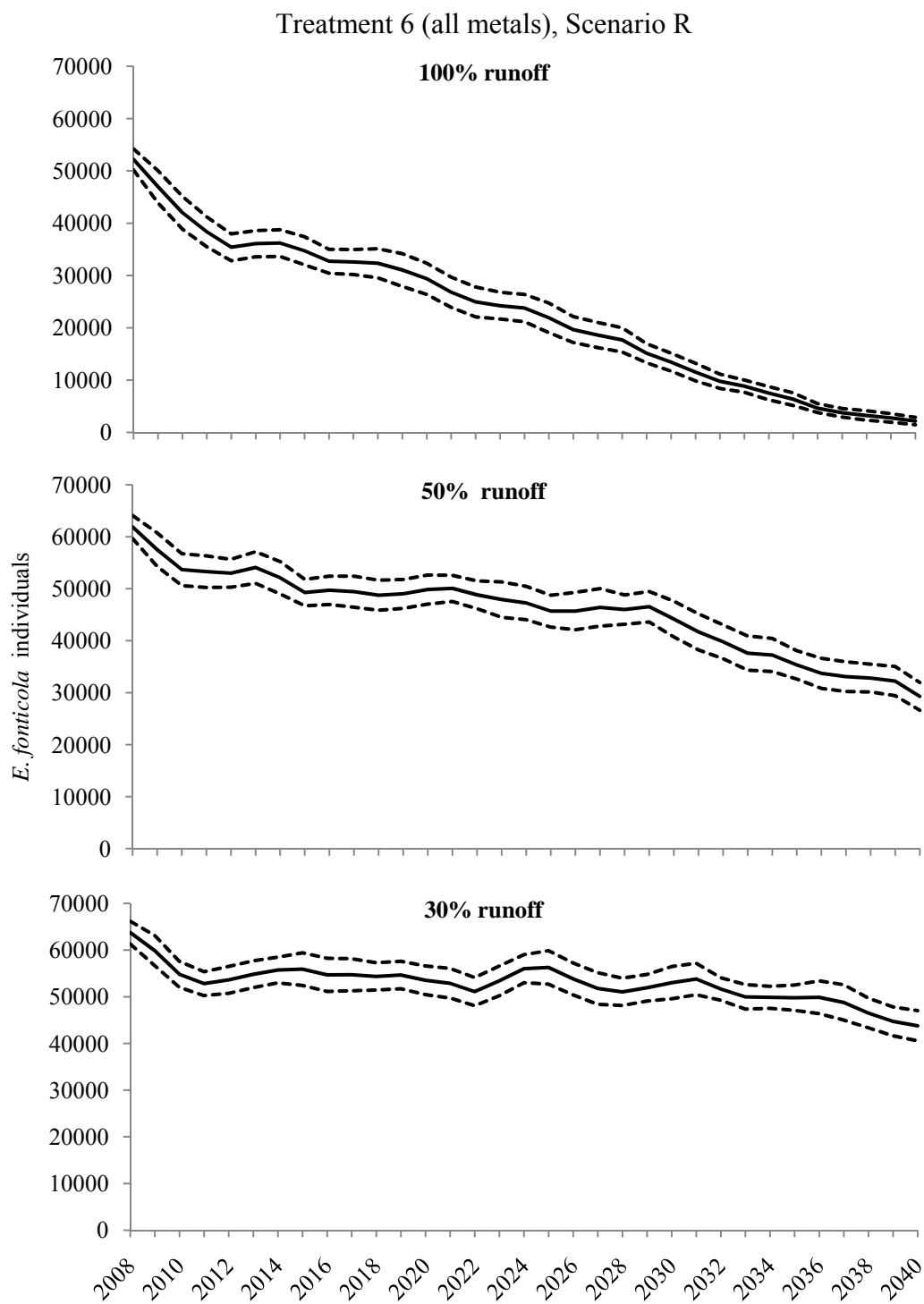


Fig. 18. Annual mean populations of *E. fonticola* under water quality with all metals, stochastic springflow and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

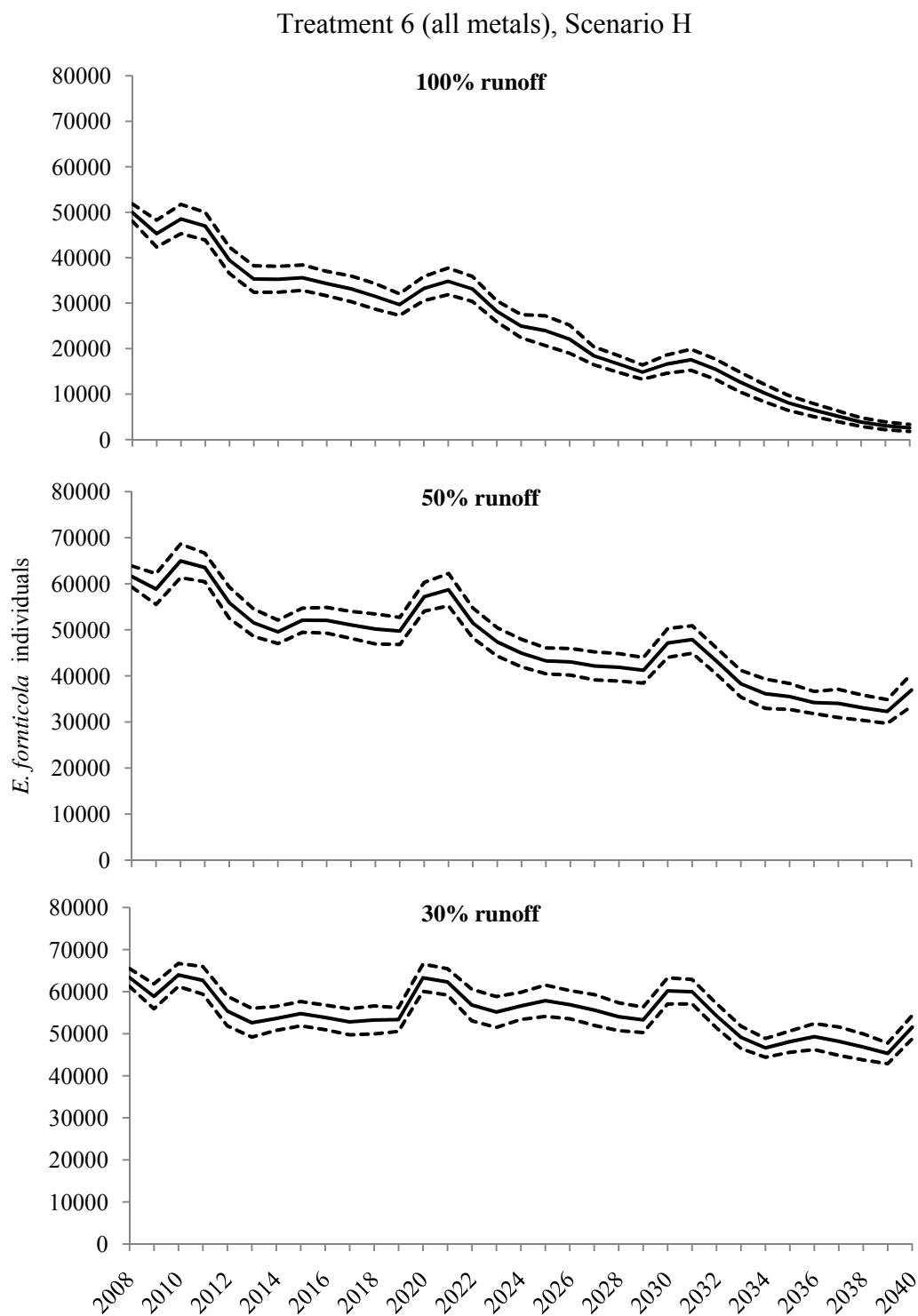


Fig. 19. Annual mean populations of *E. fonticola* under water quality with all metals, stochastic springflow with forced high flow conditions and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

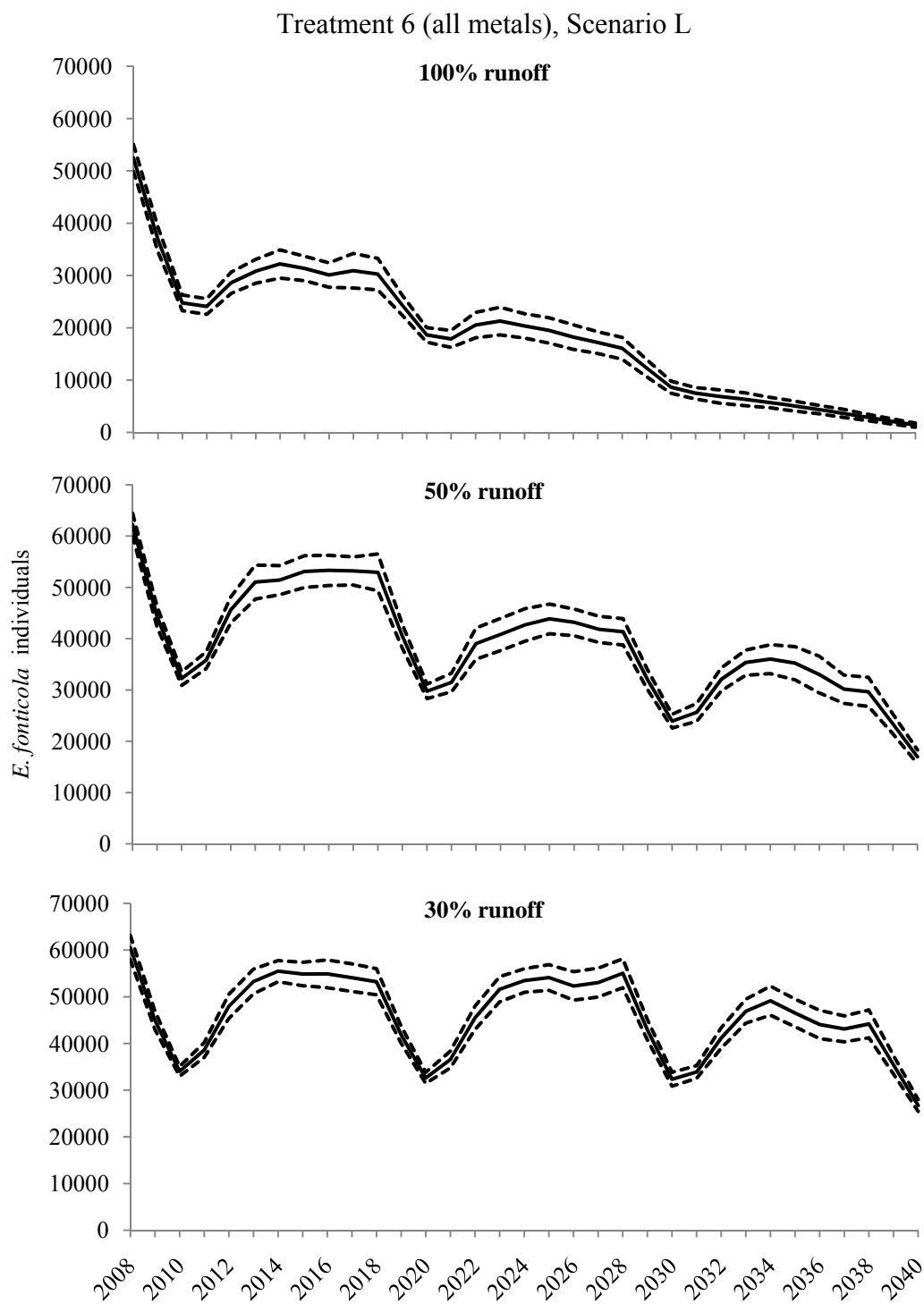


Fig. 20. Annual mean populations of *E. fonticola* under water quality with all metals, stochastic springflow with forced low flow conditions and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

Treatment 2 (copper), Scenario R

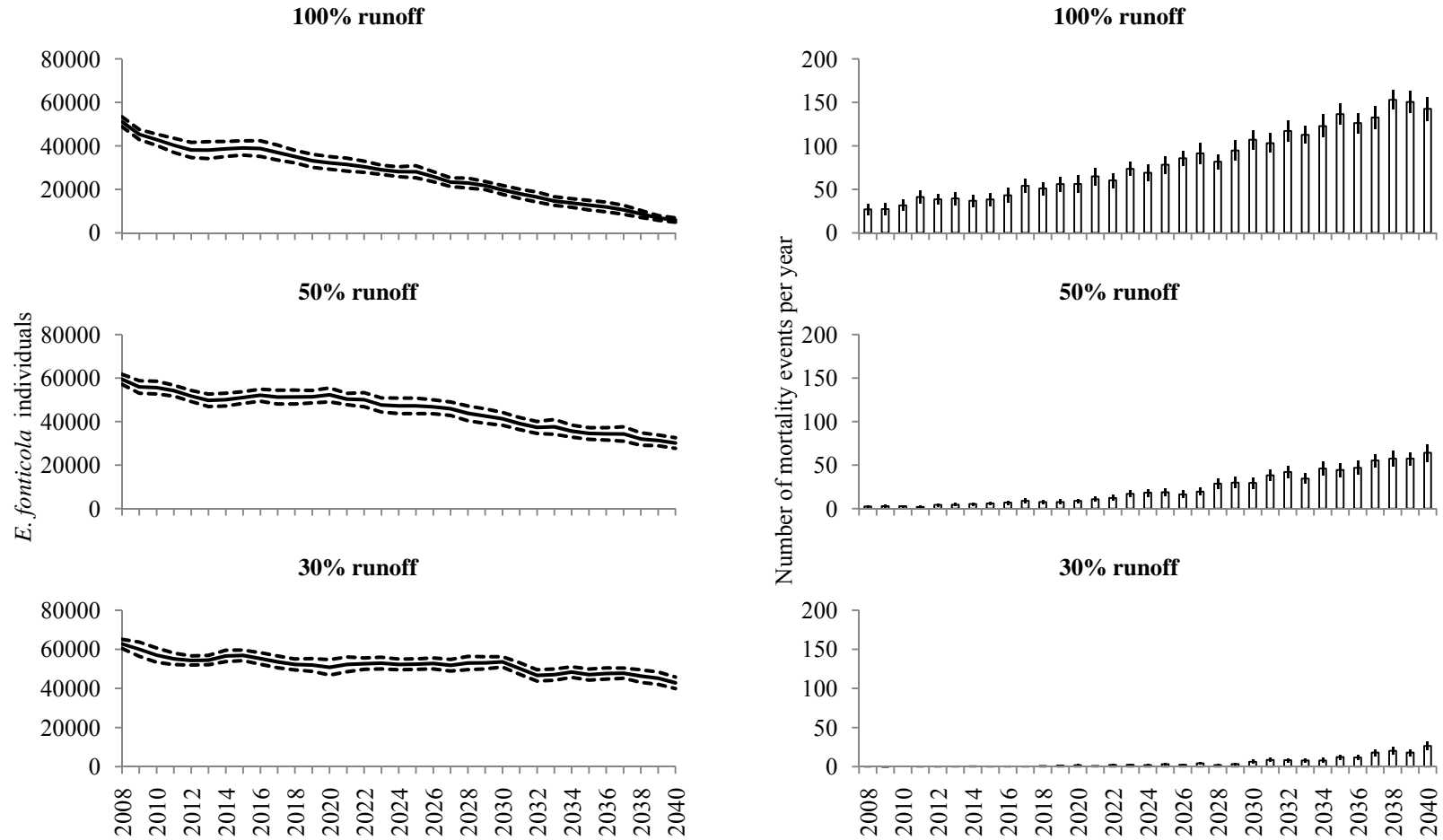


Fig. 21. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved copper exceeded chronic mortality levels (30 day average of 8.1 $\mu\text{g/L}$) (right column) for treatment 2-R. Model conditions: copper, stochastic springflows, and variation on percentage of runoff entering the San Marcos River.

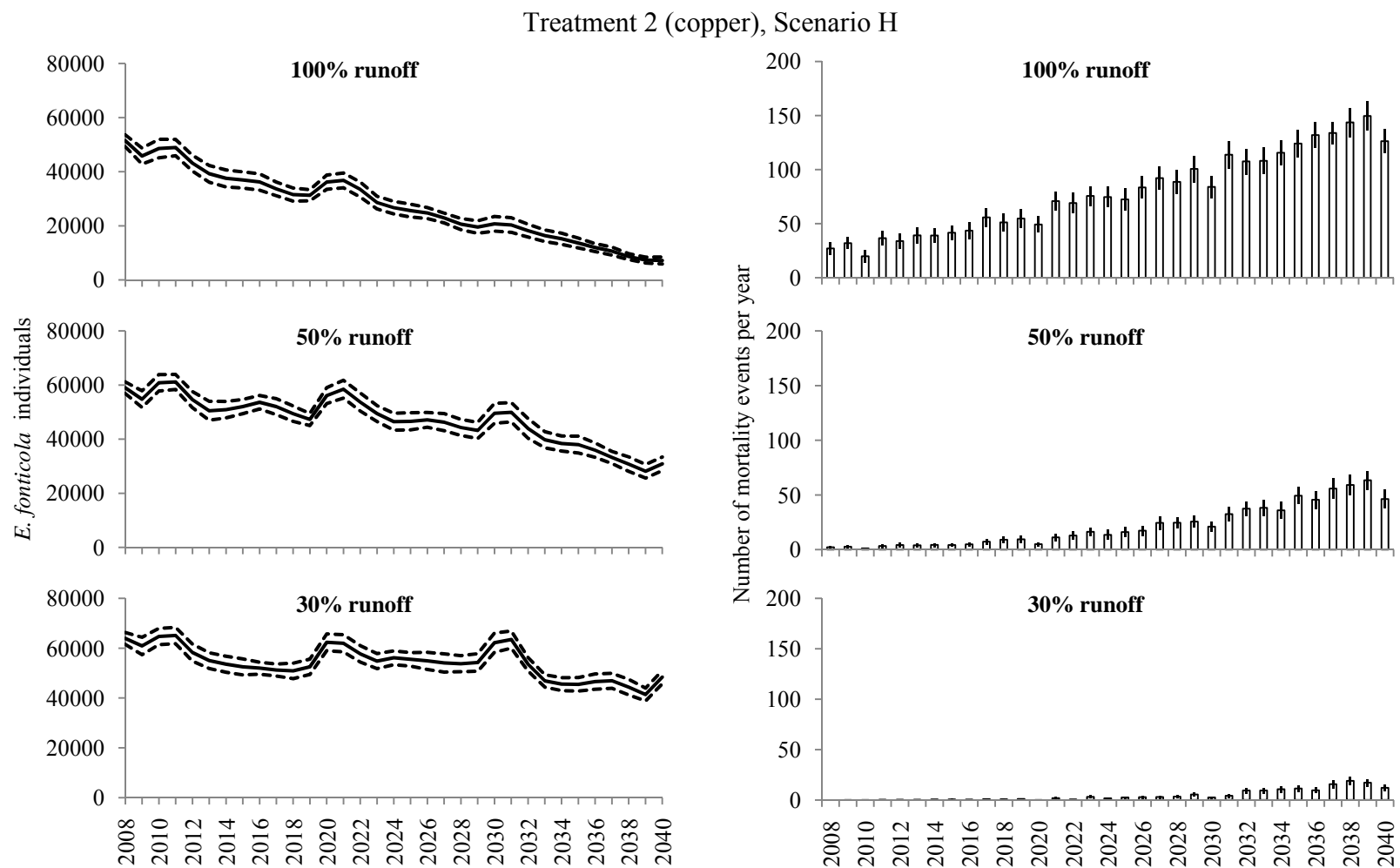


Fig. 22. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved copper exceeded chronic mortality levels (30 day average of 8.1 $\mu\text{g/L}$) (right column) for treatment 2-H. Model conditions: copper, stochastic springflows except at selected high flow years, and variation on percentage of runoff entering the San Marcos River.

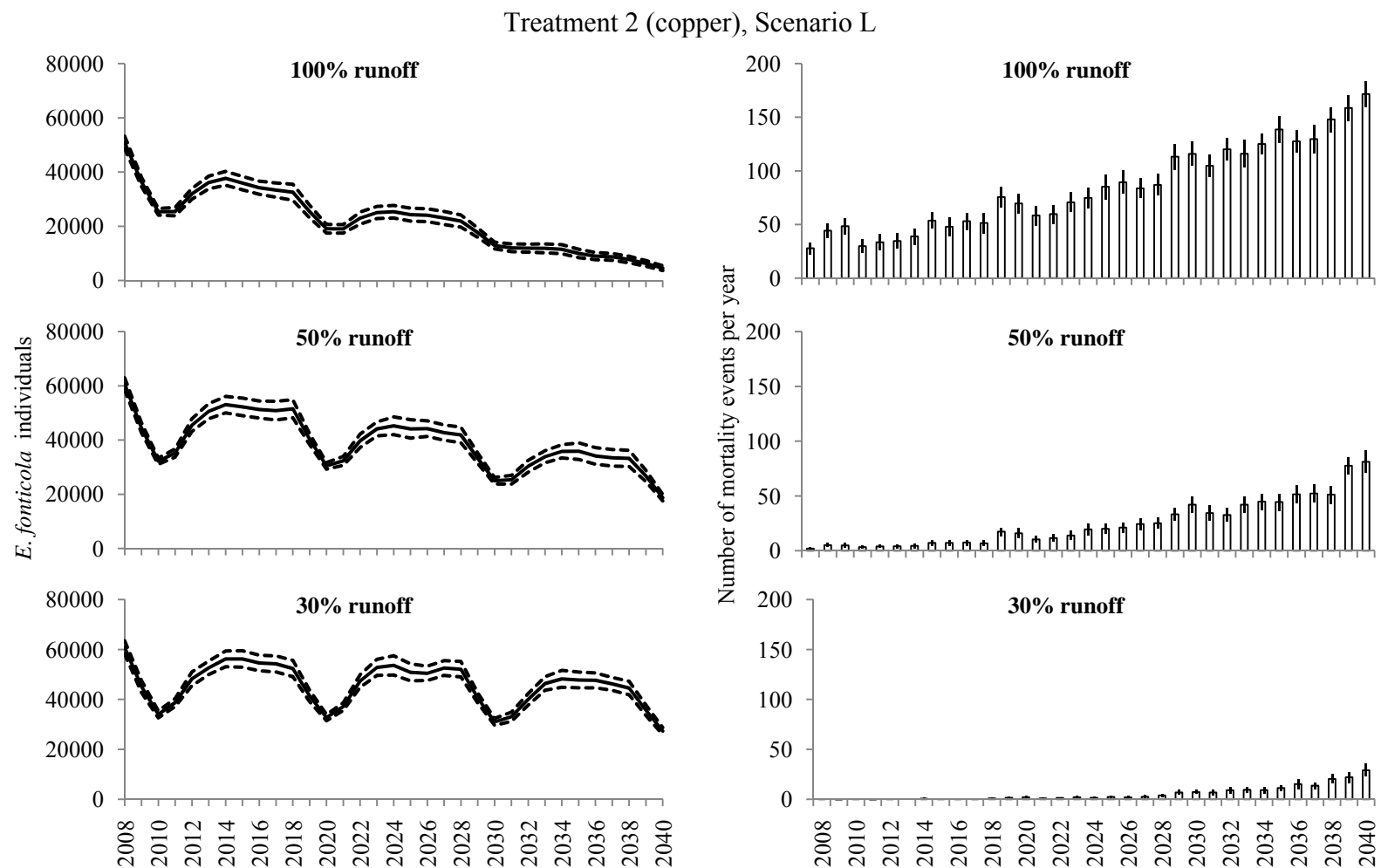


Fig. 23. Annual mean population of *E. fonticola* (dotted line=95% CI) (left column) and the average number of times levels of dissolved copper exceeded chronic mortality levels (30 day average of 8.1 $\mu\text{g/L}$) (right column) for treatment 2-L. Model conditions: copper, stochastic springflows except at selected low flow years, and variation on percentage of runoff entering the San Marcos River.

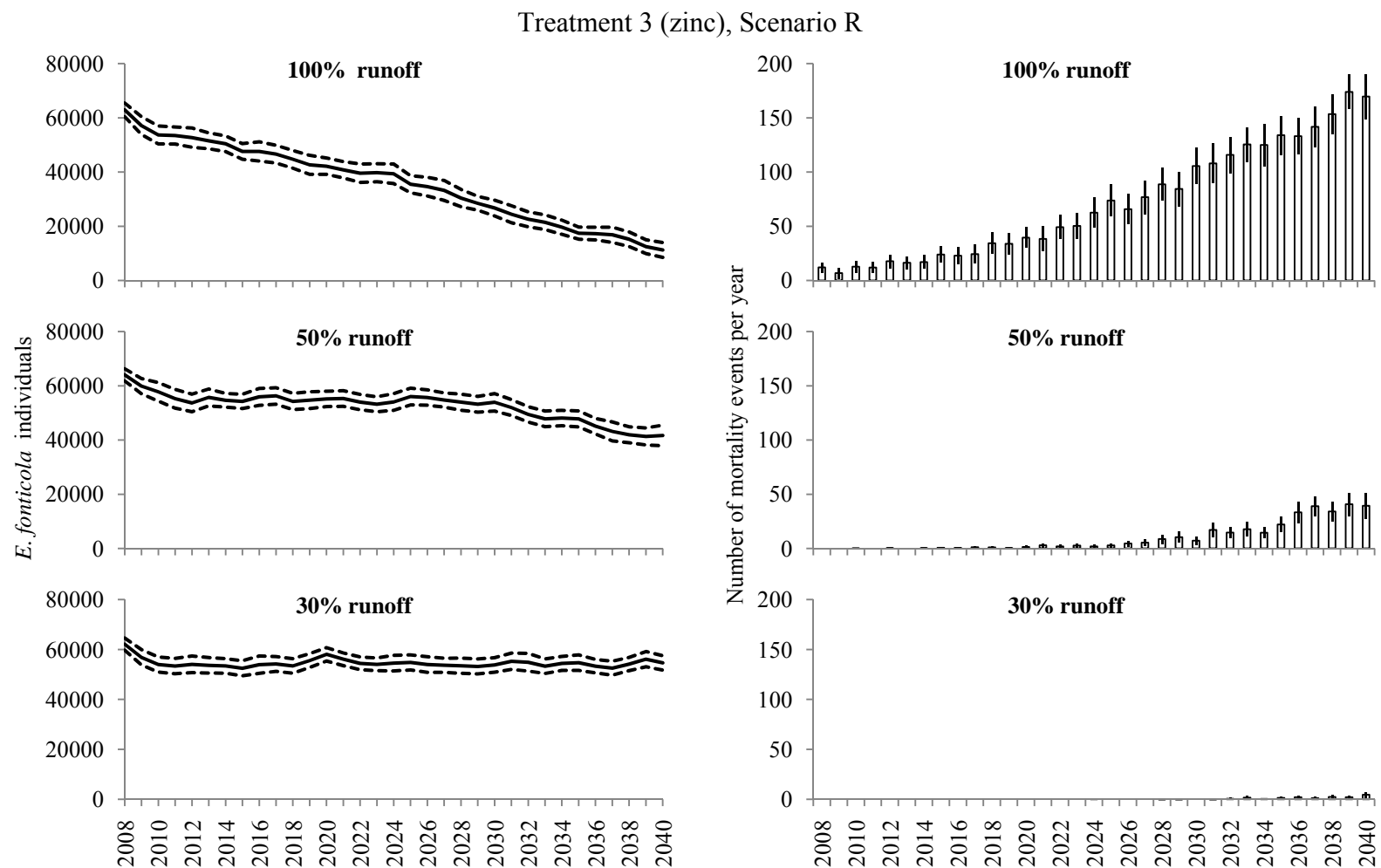


Fig. 24. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved zinc exceeded chronic mortality levels (69 day average of 88 $\mu\text{g/L}$) (right column) for treatment 3-R. Model conditions: zinc, stochastic springflows, and variation on percentage of runoff entering the San Marcos River.

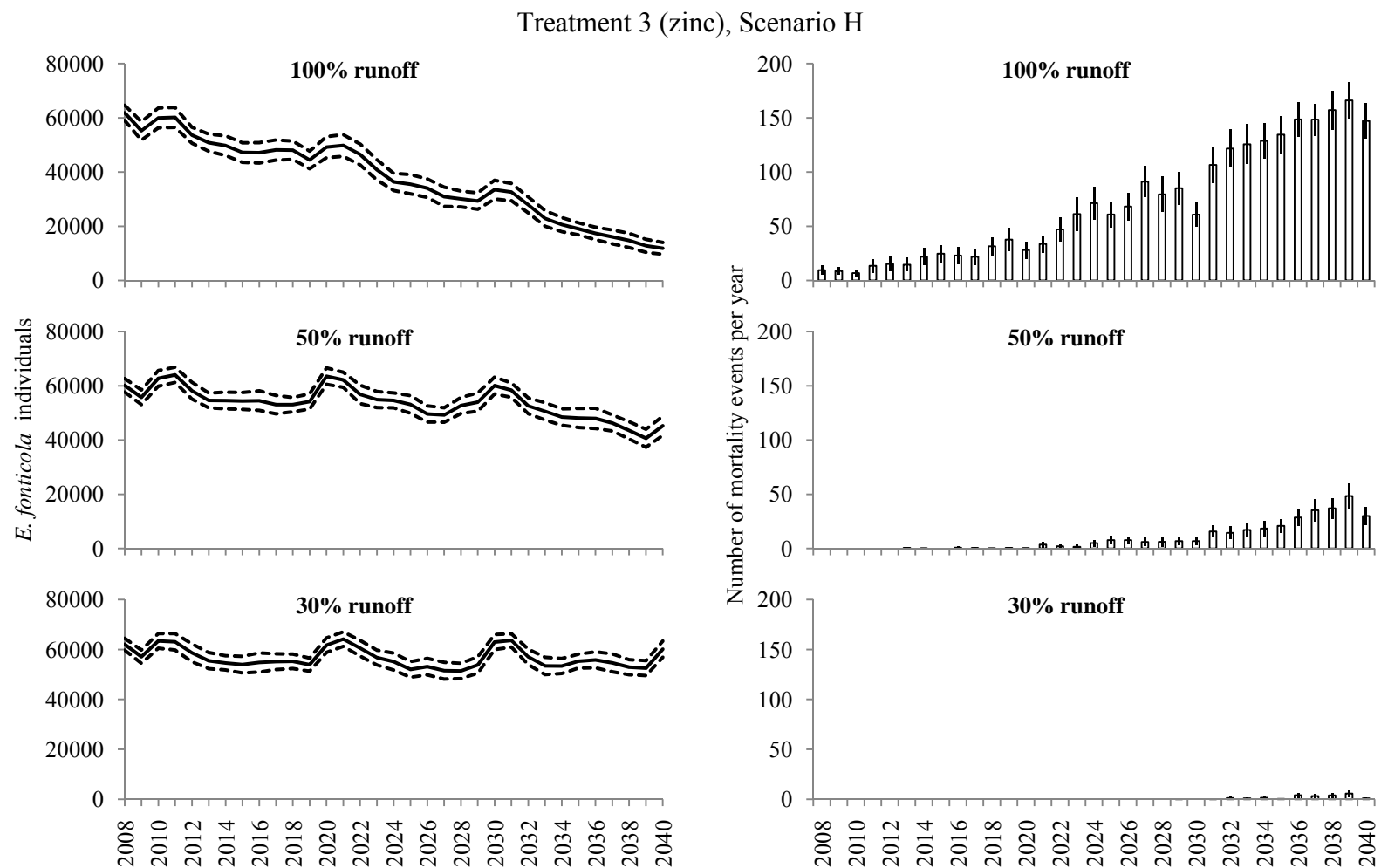


Fig. 25. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved zinc exceeded chronic mortality levels (69 day average of 88 $\mu\text{g/L}$) (right column) for treatment 3-H. Model conditions: zinc, stochastic springflows except at selected high flow years, and variation on percentage of runoff entering the San Marcos River.

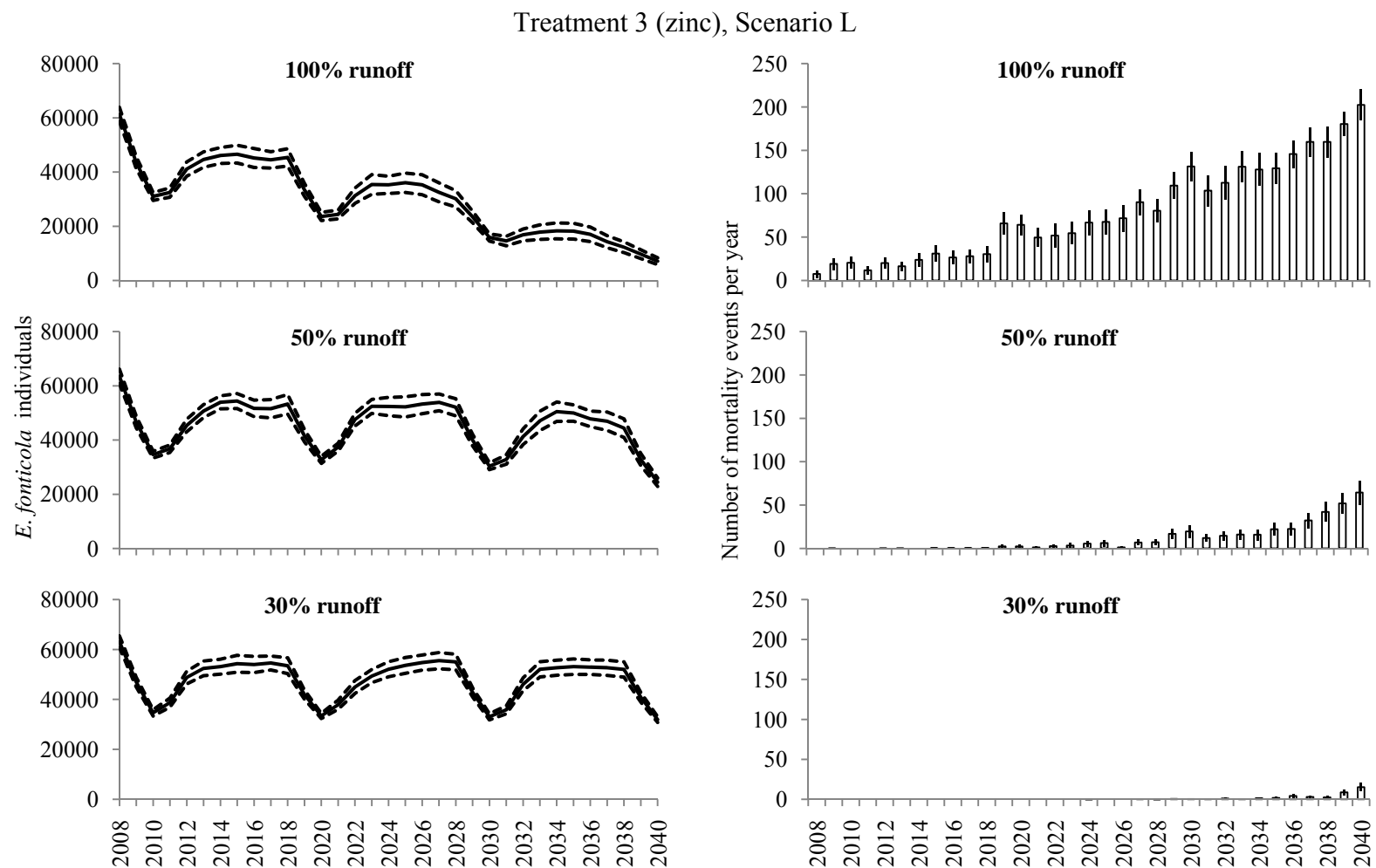


Fig. 26. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved zinc exceeded chronic mortality levels (69 day average of 88 $\mu\text{g/L}$) (right column) for treatment 3-L. Model conditions: zinc, stochastic springflows except at selected low flow years, and variation on percentage of runoff entering the San Marcos River.

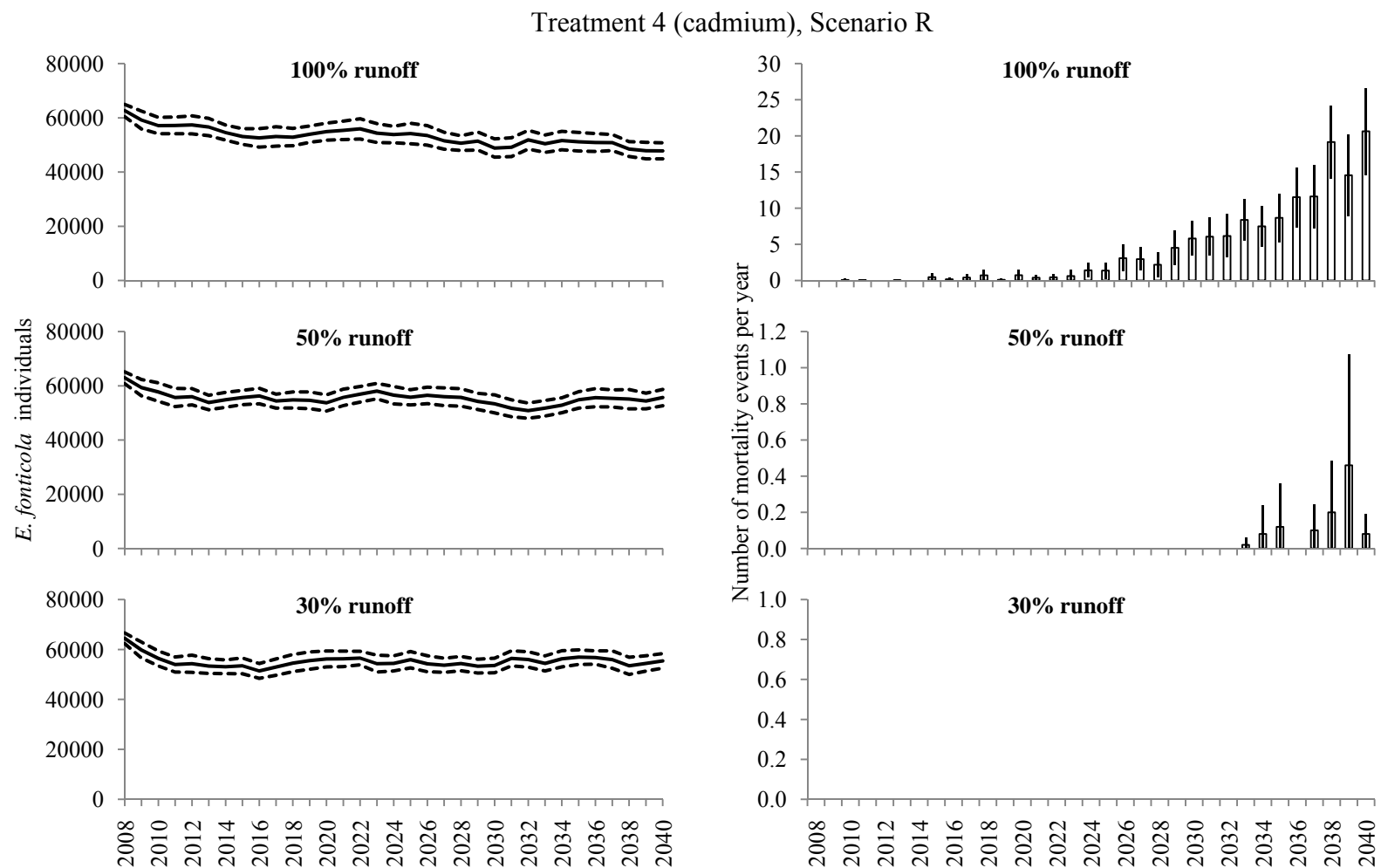


Fig. 27. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved cadmium exceeded chronic mortality levels (53 day average of 0.89 $\mu\text{g/L}$) (right column) for treatment 4-R. Model conditions: cadmium, stochastic springflows, and variation on percentage of runoff entering the San Marcos River.

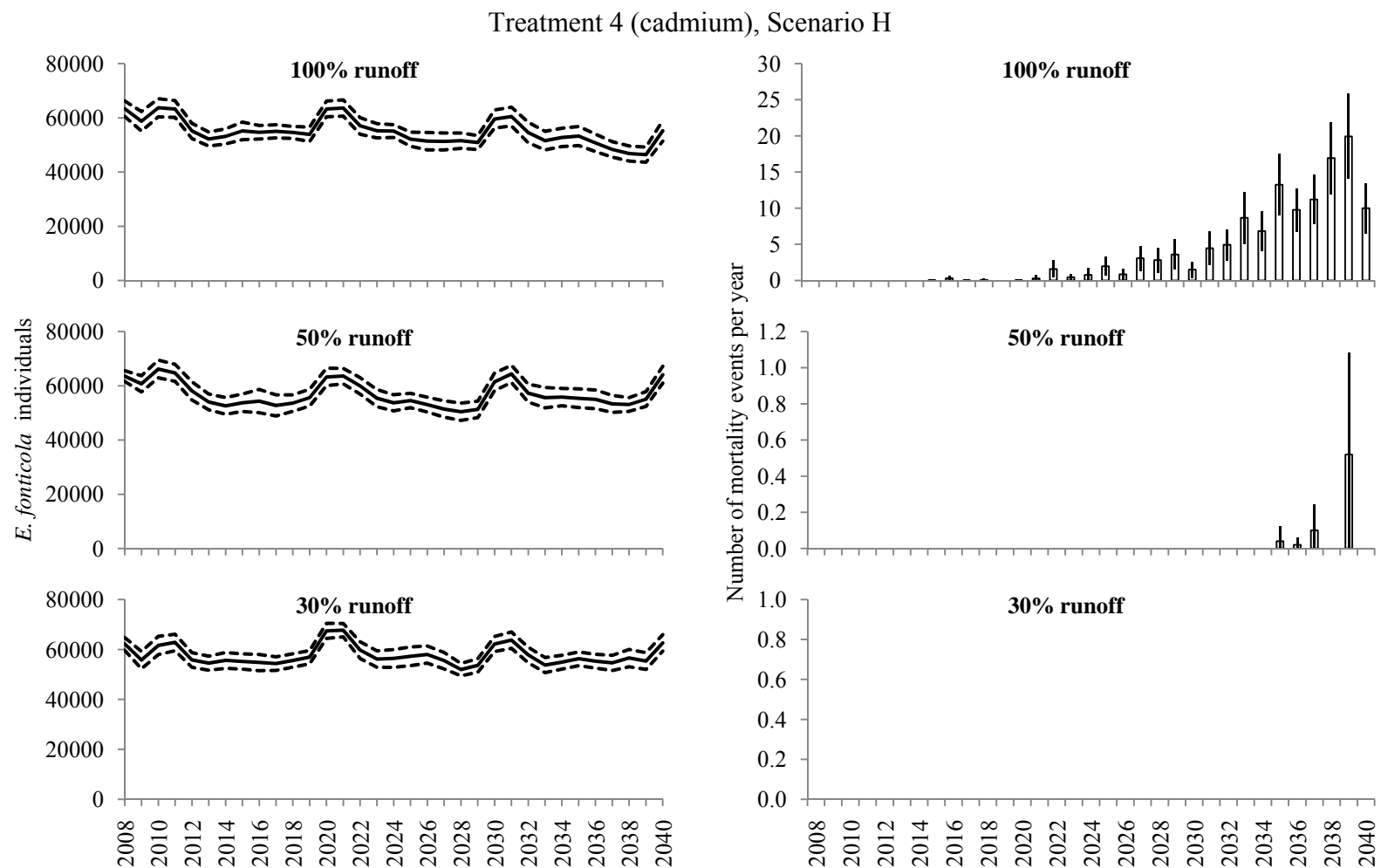


Fig. 28. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved cadmium exceeded chronic mortality levels (53 day average of 0.89 $\mu\text{g/L}$) (right column) for treatment 4-H. Model conditions: cadmium, stochastic springflows except at forced high flow years, and variation on percentage of runoff entering the San Marcos River.

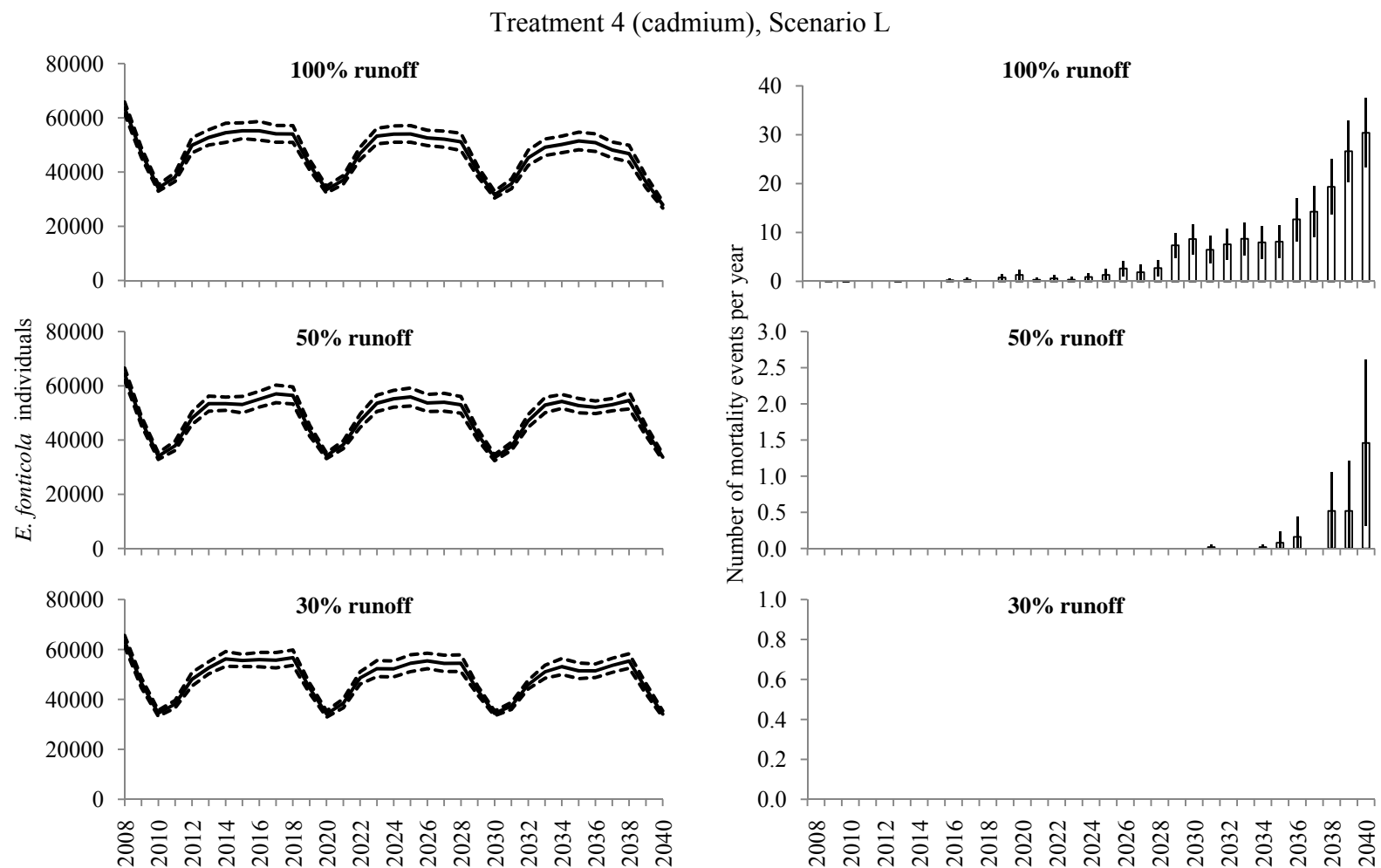


Fig. 29. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved cadmium exceeded chronic mortality levels (53 day average of 0.89 $\mu\text{g/L}$) (right column) for treatment 4-L. Model conditions: cadmium, stochastic springflows except at forced low flow years, and variation on percentage of runoff entering the San Marcos River.

Mortality events

All but chromium exceeded chronic aquatic life criterion in at least one scenario of simulations (Table 7). Dissolved concentrations of copper and zinc reached chronic mortality levels in each of the nine combinations of springflow and runoff variation while cadmium concentrations exceeded safe levels in runoff conditions > 30 percent (Figs. 21–29). The model simulated that if 100% of runoff enters the system, regardless of flow scenario, chronic levels of Cu and Zn could be exceeded already (2008). As for Cd, under high flow it modeled that by 2015 levels would have an impact on the darters and by 2020 under low flow conditions and by 2024 under the randomly generated springflow replications. Regardless of springflow scenarios, should only 30% of runoff enter the river, contaminant levels could be of concern by 2019 (Cu) and 2032–2033 (Zn).

Table 7
Simulated results for the first average year that metal water quality concentrations exceeded chronic aquatic life criteria on average at least > 1 time/year.

Scenario ^a	Cu		Zn		Cd		Cr	
	Year	MCE ^b	Year	MCE	Year	MCE	Year	MCE
R–100	2008	27.1	2008	12.06	2024	1.4	–	–
R– 50	2008	2.5	2017	1.02	–	–	–	–
R– 30	2019	1.4	2033	1.78	–	–	–	–
H – 100	2008	27.06	2008	9.5	2015	1.58	–	–
H– 50	2008	2.12	2021	3.56	–	–	–	–
H–30	2019	1.04	2032	1.24	–	–	–	–
L–100	2008	27.9	2008	7.5	2020	1.32	–	–
L–50	2008	1.92	2019	2.26	2040	1.46	–	–
L–30	2019	1.56	2032	1.12	–	–	–	–

^a R,H, L corresponds to simulated flow condition (random, high, low) respectively and 100,50,30 corresponds to the simulated percentage of runoff expected to reach the river.

^b mortality chronic event. The average (n=50) number of instances that the associated metal dissolved concentration exceeded chronic aquatic life criterion and triggered a mortality event within the model at the corresponding year. For example, the model simulated that in 2008 there were an average of 27.1 times that copper exceeded an 8.1 µg/L concentration.

Simulated last day and minimum population values

For each scenario (R, H, and L), I determined if the population by the end of the simulation (December 31, 2040) and the minimum values were different among metals. There was significant difference ($p < 0.001$, $df = 249$) between metals on the last simulated day for all scenarios: R-100 ($F = 373$), R-50 ($F = 79$), R-30 ($F = 20$), H-100 ($F = 609$), H-50 ($F = 103$), H-30 ($F = 18$), L-100 ($F = 878$), L-50 ($F = 182$) and L-30 ($F = 339$). As for the minimum values, significance was found between metals across all scenarios ($p < 0.001$, $df = 249$) as well: R-100 ($F = 752$), R-50 ($F = 98$), R-30 ($F = 11$), H-100 ($F = 827$), H-50 ($F = 93$), H-30 ($F = 11$), L-100 ($F = 1154$), L-50 ($F = 176$) and L-30 ($F = 101$).

Since the ANOVA tests indicated that population values were statistically different according to metal treatment, I then analyzed the data with Tukey's HSD tests to determine what metals caused significance. Under low flow conditions and 30 percent runoff (L-30), the all metal and copper treated population had significantly less individuals on the last simulated day and had the lowest minimum value than all the other metal treatments (all metal, copper $<$ Zn, Cd $<$ Cr). There were significantly less individuals on the lowest day (H-30, R-30) and lowest minimum (R-30) for the all metals and copper treatments (all metal, copper $<$ Zn, Cd, Cr). As for conditions of 50 percent runoff entering the river, all springflow scenarios had the least amount of individuals and the lowest minimum value under the all metals and copper treatments, followed by zinc and then cadmium and chromium treatments (all metals, Cu $<$ Zn $<$ Cd, Cr). Lastly, at 100 percent runoff conditions for high and random flow, the all metal treatment resulted in the lowest population value on December 31, 2040 (all metals $<$ Zn, Cu $<$ Cr, Cd). This was also the case for the minimum population value for H-30 scenario. The population on the last day for low flow and 100 percent runoff were all significantly different than one another: all metals $<$ Cu $<$ Zn $<$ Cd $<$ Cr. This was also the case for minimum values for all springflows at 100 percent runoff conditions.

In addition to determining that the all metal and copper treatments caused the most significant decline in populations among the metal treatments I tested if the population as of December 31, 2040 and the minimum population values simulated

under metal toxicity were significantly lower than the values simulated under clean water conditions (Chapter II). All random flow scenarios (R-100, R-50 and R-30) of each 5 metal treatments were compared to the corresponding population value (Scenario R) in clean water conditions. Similarly scenarios H-100, 50 and 30 and L-100, 50, 30 were compared to Scenarios H and L, respectively. From paired t-tests ($\alpha = 0.05$, $df = 49$), clean water conditions resulted in a significantly larger last day population for each all metal and copper scenarios; for all the zinc scenarios except at R-30 and H-30; and for all the cadmium scenarios except R-100, H-100 and L-100 (Table 8). In clean water, minimum values (Table 9) were significantly larger for all copper scenarios, all metal combination scenarios except H-30, all zinc scenarios except R-30 and H-30, and for all cadmium scenarios except R-100 and L-100.

Table 8
Exposed to metal toxicity, *E. fonticola* population values on simulated December 31, 2040 and values from paired t-test (t).

Scenario ^a	Copper		Zinc		Cadmium		All metals	
	Mean (SD)	t	Mean (SD)	t	Mean (SD)	t	Mean (SD)	t
R-100	3141 (1874) ^b	33.2	6169 (5406) ^b	22.3	27987 (6751) ^b	4.5	650 (640) ^b	37.6
R-50	16815 (6263) ^b	12.8	24684 (9365) ^b	5.4	33817 (7653)	-0.5	15740 (5455) ^b	15.6
R-30	23976 (6787) ^b	6.5	32646 (6748)	0.41	33427 (7026)	-0.2	25853 (7404) ^b	5.8
H-100	4040 (2984) ^b	35.1	6730 (4887) ^b	32.6	36182 (8375) ^c	3.6	1383 (1427) ^b	42.8
H-50	19924 (6175) ^b	15.3	28606 (8373) ^b	8.3	42166 (7027)	-0.2	23005 (8336) ^b	13.2
H-30	32722 (6236) ^b	7.3	39383 (7061)	1.8	41180 (7132)	0.6	33213 (6538) ^b	6.7
L-100	2125 (1516) ^b	53.4	3358 (2226) ^b	30.8	14958 (2525) ^b	8.0	650 (640) ^b	59.0
L-50	9420 (2434) ^b	18.7	12949 (3656) ^b	10.2	18892 (2336)	-0.3	8343 (2195) ^b	19.9
L-30	14700 (2879) ^b	8.2	17564 (2530) ^d	2.5	19126 (2538)	-0.9	14255 (3128) ^b	10.1

^a n=50

^b $p < 0.000$

^c $p = 0.001$

^d $p = 0.016$

Table 9
Exposed to metal toxicity, *E. fonticola* minimum population values and paired t-test (t) results.

Scenario ^a	Copper		Zinc		Cadmium		All metals	
	Mean (SD)	t	Mean (SD)	t	Mean (SD)	t	Mean (SD)	t
R -100	2289 (1266) ^b	43.9	3912 (2709) ^b	28.7	17003 (2798) ^b	4.1	572 (544) ^b	47.9
R- 50	11569 (2702) ^b	14.9	15585 (3097) ^b	6.2	19472 (3246)	0.1	10963 (2894) ^b	15.0
R - 30	16931 (2899) ^b	4.4	19100 (3176)	0.7	191770 (3047)	0.6	16370 (2795) ^b	5.4
H - 100	2671 (1391) ^b	37.5	4203 (2233) ^b	28.3	18288 (2609)	1.4	1022 (1026) ^b	37.8
H- 50	11687 (2917) ^b	11.1	16217 (2962) ^b	5.0	19376 (2698)	-0.5	11713 (2632) ^b	11.9
H-30	17084 (2977) ^c	2.9	19058 (2789)	-0.0	19626 (2824)	-1.0	18037 (2614)	1.6
L-100	1773 (1002) ^b	50	2702 (1600) ^b	36.8	13284 (1769) ^b	6.7	572 (544) ^b	55.4
L-50	8430 (1699) ^b	19.8	11388 (2513) ^b	10.5	15695 (2083)	0.2	7630 (1819) ^b	21.8
L-30	13135 (2155) ^b	7.2	14726 (1315) ^d	3.5	15754 (2167)	0.1	12696 (2253) ^b	7.9

^a n=50

^b p < 0.000

^c p = 0.005

^d p = 0.001

CHAPTER IV

IMPACT OF ORGANICS

Introduction

This chapter describes the final set of simulations assessing to what degree water quality changes, specifically organic contaminants, might affect the Upper San Marcos River fountain darters. To model organics in the system I built upon those submodels discussed in the previous two chapters. Within this chapter, I first present a brief overview of the organics chosen, PAH and pesticides, and their toxic properties within aquatic environments. This is followed by quantitative description of the submodels related to PAHs and to pesticides. I then conclude with a summary of the simulations and results for all organics.

Background: phenanthrene, dicamba, carbaryl, bifenthrin

Besides metals, our urban waterways often contain organic chemicals. An organic contaminant can be naturally occurring or a synthetic chemical such as herbicides, pesticides or may even be a byproduct of industrial processes. I selected four to model and represent potential toxicity to fountain darters: (1) phenanthrene, (2) dicamba, (3) carbaryl, and (4) bifenthrin. These four compounds met the following selection requirements. First, the majority of their deposition occurs within urban settings. Secondly, there is substantial documentation of their presence and accumulation within urban streams and rivers. Finally, they are potentially toxic to aquatic organisms, specifically the fountain darter.

Organics are classified according to structure and one compound class of concern for the fountain darters are polycyclic aromatic hydrocarbons (PAHs) (White et al., 2006). These compounds are made of hydrogen and carbon that form into two or more benzene rings (Eisler, 1987). Sources of PAHs include natural combustion like forest fires and volcanoes or anthropogenic combustion sources like fossil fuel (Newman and Unger, 2003). Quantities of PAHs in water have been traced back to nearby deposition sources, especially urban areas (Eisler, 1987). Vehicles that travel on paved residential

streets, highways or interstates, leave behind organic polycyclic aromatic hydrocarbon residue from fuel combustion and oil spills (MacKenzie and Hunter, 1979; Hoffman et al., 1984). This residue is subject to runoff and thereby can enter the waterways and become potentially toxic to the aquatic species but because PAHs are hydrophobic, they adhere to dust particles and thus make their way to surface water via runoff sediment (Herrmann, 1981). For example, streams in Dallas–Fort Worth contained 24 different PAHs (Moring and Rose, 1997) and sediment in the San Marcos River had concentrations of PAHs including fluoranthene and pyrene (White et al., 2006). Pyrene, fluoranthene and phenanthrene account for the majority of PAH toxicity in extracted sediments of urban streams (Boxall and Maltby, 1997) but only phenanthrene has established water quality recommendations (White et al., 2006). Thus, I selected phenanthrene to model as representative of PAH toxicity on fountain darters.

Besides PAHs, pesticides have been detected in Edwards Aquifer wells (White et al., 2006). In fact, seventy to ninety percent of households in the United States use pesticides for lawn care and insect control (Paul and Meyer, 2001). For example, in a study of eight urban streams around the U.S., Hoffman et al. (2000) reported that 97 percent of their samples contained at least one herbicide and 89 percent at least one insecticide. Recently, carbaryl levels exceeding aquatic life criterion have been detected in urban waters (Liu et al., 2004; Weston et al., 2009) and dicamba and bifenthrin levels have been detected in California urban areas (Weston et al., 2009).

Dicamba is an herbicide often applied directly to the foliage of trees and plants. It is the least toxic of the three pesticides with a LC₅₀ (96 h) equal to 135 mg/L for rainbow trout (Exttoxnet, 2008). It was detected in New York urban runoff at levels > 1 µg/L and in the same study carbaryl exceeded the aquatic life criterion (Phillips and Bode, 2004).

Carbaryl (a carbamate insecticide) is the active ingredient in several lawn care and agricultural insecticides with popular chemical trade names like Sevin®, Bugmaster® and Tercyl® (Exttoxnet, 2008). Up to 75% of carbaryl lost to runoff is in the water, the remainder adheres to sediment particles (Caro et al., 1974). In an urban

stream study, carbaryl (with a 44% detection frequency) exceeded the aquatic life criterion ($0.2 \mu\text{g/L}$) 10% of the time sampled (Hoffman et al., 2000). In water, it has a half-life of 10 days, making it moderately toxic to aquatic organisms such as rainbow trout ($\text{LC}_{50} (96 \text{ h}) = 1.3 \text{ mg/L}$) (Extoxnet, 2008).

The third pesticide chosen to model was bifenthrin. It is an insecticide but more toxic to the aquatic ecosystems than carbaryl (rainbow trout, $\text{LC}_{50} (96 \text{ h}) = 0.00015 \text{ mg/L}$) (Extoxnet, 2008). It is a pyrethroid, which are increasingly replacing organophosphate insecticides for household pest control (Raloff, 2006; Weston et al., 2009). In a California assessment, bifenthrin, applied mostly to yards, was detected in 23 out of 24 water/sediment samples (mean $5\text{--}17 \mu\text{g/L}$) (Weston et al., 2009). Similar to PAHs it tends to be hydrophobic suggesting that the majority of bifenthrin entering the system is bound to the sediment. However, 10–27% of bifenthrin in runoff is dissolved and bioavailable and thus has the potential to affect aquatic organisms (Liu et al., 2004).

In summary, I chose four organic compounds to model and they all have a potential to cause impacts on the fountain darter and are present in urban areas, even some in the Edwards Aquifer. I wanted to determine what might be their impacts into the future in association with impervious area and thus continued to develop the fountain darter population dynamics model (Fig. 30).

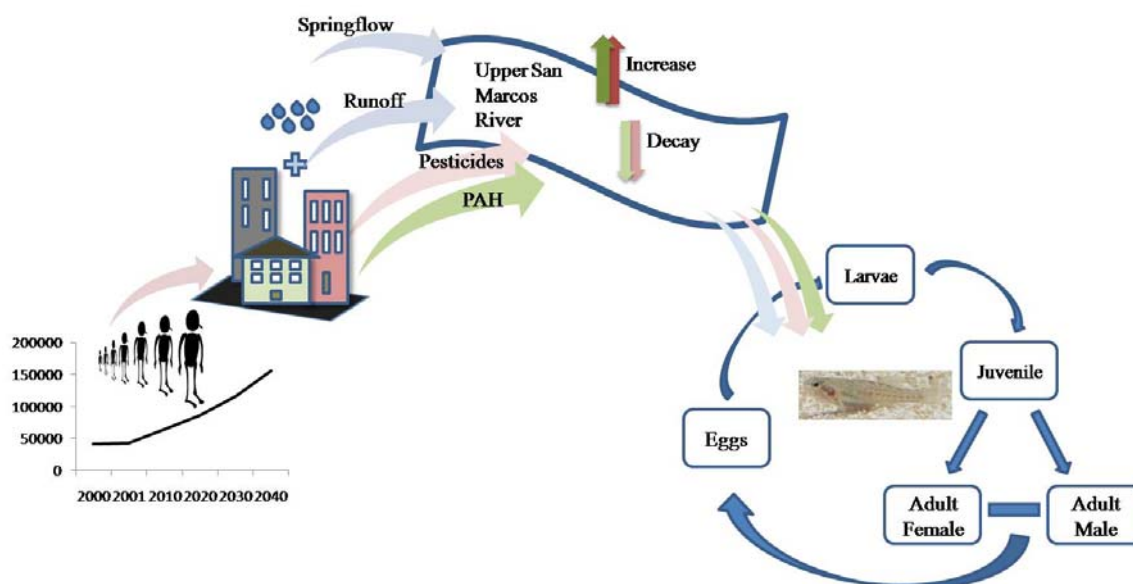


Fig. 30. Conceptual model of how organics includes pesticides and PAH enter the Upper San Marcos River and its impact upon the fountain darter population.

Quantitative model description: PAH

PAHs have high adsorption rates to runoff sediment. To model the bioavailable PAH levels in the San Marcos, I developed two submodels to determine fountain darter ingestion and excretion of phenanthrene. These are in addition to the runoff, contamination concentration and contaminant decay submodels of Chapter III.

Runoff

See Chapter III.

Contaminant concentration

See Chapter III. The estimated mean concentration of PAH is different than the metals (Menzie et al., 2002).

Contaminant decay

This submodel calculates the amount of phenanthrene entering the river that is bioavailable. The differences from the metal contaminant decay submodel in Chapter III are described hereafter. The daily dissolved concentration ($\mu\text{g/L}$) of phenanthrene is a factor of incoming concentration at time t (SMPc) and the decay rate as determined by

phenanthrene's half-life in water, equal to 2 hours (Fujiwara et al., 2007). The concentration at the end of day 1 is then added to the incoming concentration at $SMPc_{t+1}$. This way the concentration of phenanthrene in the water is subject to decay and accumulation over time. The bioavailable phenanthrene at time t is represented by Pcw_t .

PAH ingestion

Since the amount of dissolved phenanthrene is limited, I wanted to account for any bioaccumulation that might occur through diet, therefore this submodel accounts for ingestion of phenanthrene via gill and dietary uptake. It simulates the concentration of phenanthrene entering fountain darter tissues at time t and at life stage s (larvae, juvenile, adult, or adult 2). Table 10 summarizes model parameters for phenanthrene ingestion.

The concentration of phenanthrene within a fountain darter at life stage s ($\mu\text{g PAH/kg fish/d}$) is the sum of accumulation via gill uptake and food ingestion (G_u and D_u , respectively) ($\mu\text{g PAH/kg fish/d}$). G_u is determined by multiplying the gill uptake rate (k_u) (equal to 626 L of water/kg fish/d) by the dissolved PAH concentration, Pcw_t ($\mu\text{g PAH/L of water}$). D_u is determined by multiplying the dietary uptake rate (kd_t) (equal to 0.17 kg food/kg org/d) by Pcd_t , the PAH concentration within the diet ($\mu\text{g PAH/kg of food}$).

The fish are stationary feeders that have a selective diet consisting of insects, microcrustaceans, and some vegetation but preferences vary according to life stage and season (Schenck and Whiteside, 1977a). The model calculates the concentration of PAH in the diet via the following equation:

$$Pcd_t = (ap_s * Pca_t) + (ip_s * Pci_t) \quad (16)$$

where ap_s is the proportion of amphipods in the diet at life stage s (Fig. 31); Pca_t is the concentration of PAH in amphipods at time t ; ip_s is the proportion of aquatic insects in the diet at life stage s (Fig. 32) and Pci_t is the concentration of PAH in aquatic insects at

time t . To determine the concentration of phenanthrene in amphipods and aquatic insects I used the following equation (Watanabe et al., 2005):

$$Pc_{ai} = L_{ai} * K_{ow} * Pc_{wt} \quad (17)$$

where L_{ai} is the lipid fraction of amphipods or insects (1.8%, 5.0% respectively); K_{ow} is the octanol-water partition coefficient (37200 for phenanthrene) and Pc_{wt} is the dissolved PAH concentration in water ($\mu\text{g PAH/L}$) at time t .

Table 10
Base-level model parameters of fountain darter phenanthrene ingestion.

Model Notation	Parameter	Value	Source
L_a	Lipid fraction of amphipods	5.0%	Watanabe et al., 2005
L_i	Lipid fraction of aquatic insects	1.8%	Watanabe et al., 2005
K_{ow}	Octanol-water partition coefficient of phenanthrene	3.72×10^4	Watanabe et al., 2005
ap_s	Proportion of amphipods in fountain darter diet at life stage s	Fig. 31	Scalet, 1972; Schenck and Whiteside, 1977a
ip_s	Proportion of aquatic insects in fountain darter diet at life stage s	Fig. 32	Scalet, 1972; Schenck and Whiteside, 1977a
ku	Water uptake rate constant ^{a, b}	646	Baessant et al., 2001
kd	Dietary uptake rate constant ^{a, b}	0.17	Watanabe et al., 2005

^a Based on rainbow trout, no data available for fountain darters

^b Assumed constants to be equal at all life stages

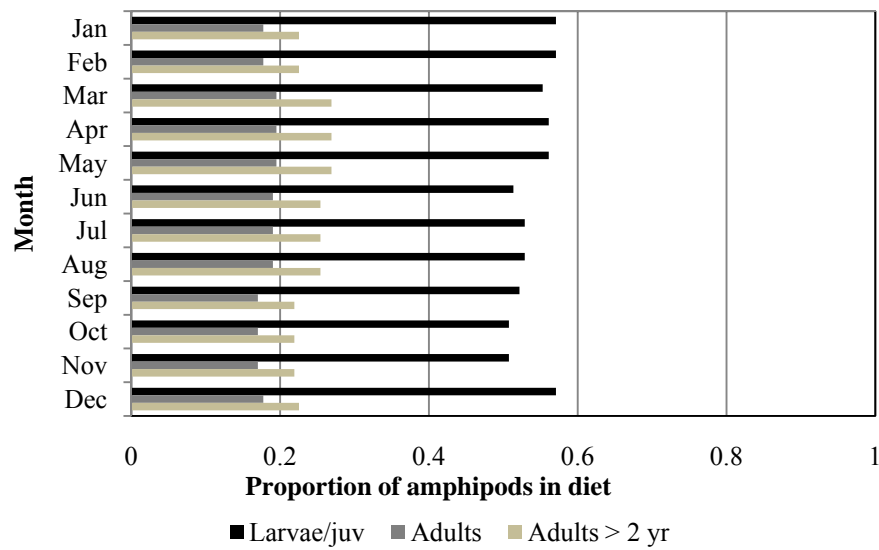


Fig. 31. Proportion of amphipods in all post-hatch fountain darter life stage diets.

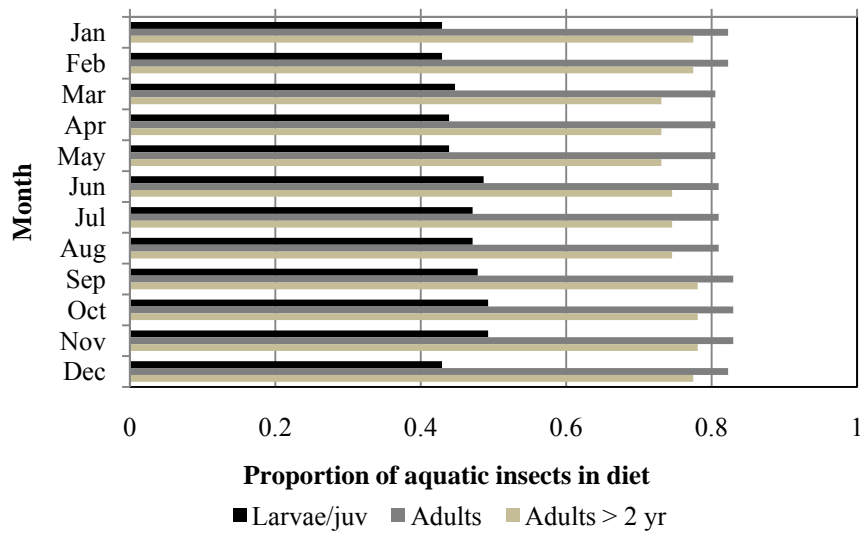


Fig. 32. Proportion of aquatic insects in all post-hatch fountain darter life stage diets.

PAH excretion and associated mortality

Once phenanthrene is ingested by the darter, this submodel quantifies its accumulation and excretion within the fish tissues. Pf_t is the ingested PAH concentration ($\mu\text{g PAH/kg org/d}$) at time t . On day 1, it enters into the body (Pin) and is subject to an elimination rate constant equal to 0.69 (Baussant et al., 2001). The amount of PAH in the tissue at time t is equal to Pt_t . That value is retained if time $t > 1$ then Pin_{t+1} is equal to the sum of Pf_t and Pt_t . If Pt_t , at life stage s , is greater than or equal to $4307 \mu\text{g PAH/kg org/d}$ then 50% of the population of life stage s at time t will die. To determine what the water quality tissue level criterion was for phenanthrene I multiplied the water quality chronic value ($4.6 \mu\text{g/L}$, White et al., 2006) by the bioconcentration factor (936 L/kg org , Baussant et al., 2001). The bioconcentration factor was determined by dividing the water uptake constant rate (646 L/kg org) by the total elimination rate constant (0.69). Any mortality becomes additive to at life stage s model parameters Lm , Jm , Fm , Mm , $F2m$ or $M2m$ (Chapter II).

Quantitative model description: organic pesticides

The runoff, contaminant concentration and decay submodels of Chapter III are modified to simulate organic pesticide contamination of the San Marcos River.

Runoff

Bifenthrin, carbaryl, and dicamba are organics that are applied to areas of vegetation. Therefore, unlike metals, impervious area cannot be used as an indicator of application. I assumed that the inverse percentage cover of impervious surfaces would adequately describe the area available for pesticide use. Thus runoff associated to areas of pesticide application is a function of the percentage of pervious area and the soil moisture content at time t .

Pervious area

The following equation is used to determined the percentage of the sub-basin that is available for the application of pesticides (PA):

$$PA_t = (1 - TIA_t) * A \quad (18)$$

where TIA_t is impervious area at time t calculated by Eq. 12 and A is the area of the sub-basin in acres.

Runoff

Once the area of the sub-basin available to pesticide application is calculated, the model predicts annual runoff in acre-inches per year using the Curve Number method as described by the following:

$$Q_t = [(P_t - 0.2S)^2 / (P_t + 0.8S)] * PA_t \text{ where,} \quad (19)$$

$$S = (1000/CN) - 10 \quad (20)$$

where P_t represents the annual rainfall depth in inches at time t (replicated from random selection of annual rainfall values for 1973-2007); S is a parameter where CN is the curve number. To determine the CN , I assumed the pervious area would be good conditioned lawns and pastures with antecedent soil moisture content (AMC) II. The soil type in the sub-basin is mostly clay (Houston black clay 39.1%, Houston gravelly clay 14.7 %, and Crawford stony clay 5.7%, Crawford silt clay 5.5%) (Mangum and Lyman, 1906). Therefore, CN is equal to 80. To use the NRCS curve number precipitation must be greater than $0.2S$ else runoff (Q) is equal to 0.

Contaminant concentration

The contaminant load submodel determines the dissolved concentration of a pesticide as a factor of the runoff and springflow volumes. The equations (13-15) are the same as in the chemical concentration submodel of metals: ACL_t becomes AOL_t (annual organic load in pounds), DCL_t becomes DOL_t (daily organic load in μg) and SMC_c becomes SMO_c (dissolved concentration of organics in $\mu g/L$).

Contaminant decay

The contaminant decay model determines the quantity of an organic as it accumulates or decays over time and calculates when levels in the water exceeds a chronic mortality levels for fountain darter larvae.

To calculate daily dissolved concentrations of carbaryl, dicamba, and bifenthrin the levels ($\mu\text{g/L}$) are factors of the concentration within the river at time t and their respective decay rate as determined by half-life in water (Ol). The average concentration is taken over a designated time (Oa), dependent upon the pesticide, and if that exceeds a specific threshold then a larvae mortality event is triggered (Om). The parameters for the organic pesticide used in the model are summarized in Table 11.

Table 11
Base-level half live and chronic toxicity levels for pesticide parameters.

Chemical	Model Notation	Value	Source
Bifenthrin	Ol ^a	26 days (0.0263)	Hornsby et al., 1996
	Oa ^b	0.15 $\mu\text{g/L}$ per 4 days ^c	Exttoxnet, 2008
	Om ^c	0.5	Exttoxnet, 2008
	EMC ^d	0.0073 $\mu\text{g/L}$	Weston et al., 2009
Carbaryl	Ol	10 days (0.0669)	Exttoxnet, 2008
	Oa	2020 $\mu\text{g/L}$ per 4 days ^f	Dwyer et al., 2005
	Om	0.5	Dwyer et al., 2005
	EMC	0.003 $\mu\text{g/L}$	CWP, 2003
Dicamba	Ol	7 days (0.0943)	Exttoxnet, 2008
	Oa	135000 $\mu\text{g/L}$ per 4 days ^e	Exttoxnet, 2008
	Om	0.5	Exttoxnet, 2008
	EMC	1.8 $\mu\text{g/L}$	CWP, 2003

^a Half-life dissolved in water

^b Average contamination level not to be exceeded

^c Mortality rate upon contamination exceeded

^d Runoff event mean concentration

^e LC50 for rainbow trout, 96 h duration

^f LC50 for fountain darter, 96 h duration

Simulation of organic toxicity on *E. fonticola*

To predict future impacts on the San Marcos system from organic compounds, I simulated water quality conditions under four treatments: a polycyclic aromatic hydrocarbon and three pesticides. The modeled river was contaminated by one organic at a time (treatments 7-10). Each treatment was simulated nine times; each a different combination of springflow and percent runoff entering the river (R-100, 50 or 30; H-100, 50 or 30; and L-100, 50, or 30). There were four predictions of interest: (1) the population trend over the simulation period (2008–2040), (2) average number of times dissolved pesticide concentrations exceeded the chronic aquatic life criterion for each simulated year, (3) the population value on the last simulated day (December 31, 2040) and (4) the minimum population value over the entire simulated period.

Simulated population trends

Of the organics, phenanthrene (PAH) had the greatest impact upon the darter population (Fig. 33-35). At 100% runoff levels, the darter population declines from nearly 40,000 individuals in 2008 to less than 5,000 individuals by 2040 under the low flow scenario. At 50% runoff, the population declined at a decreased rate, the range extending from 60,000 individuals in 2008 to less than 20,000 individuals by 2040 under the low flow scenario. At 30% runoff, the population was mostly stable, hovering at 50,000. None of the pesticides had any impact upon the population, and so population trends were similar to those evaluated for clean water conditions. Exposed to PAHs, the simulated population fell below 23,000 (half of the most recent estimate of ~46,000, Linam (1993)) by 2021 under random flow and 100% runoff, by 2026 at with forced high flows and 100% runoff and by 2019 with forced low flow conditions at 100% runoff (Fig. 33-35).

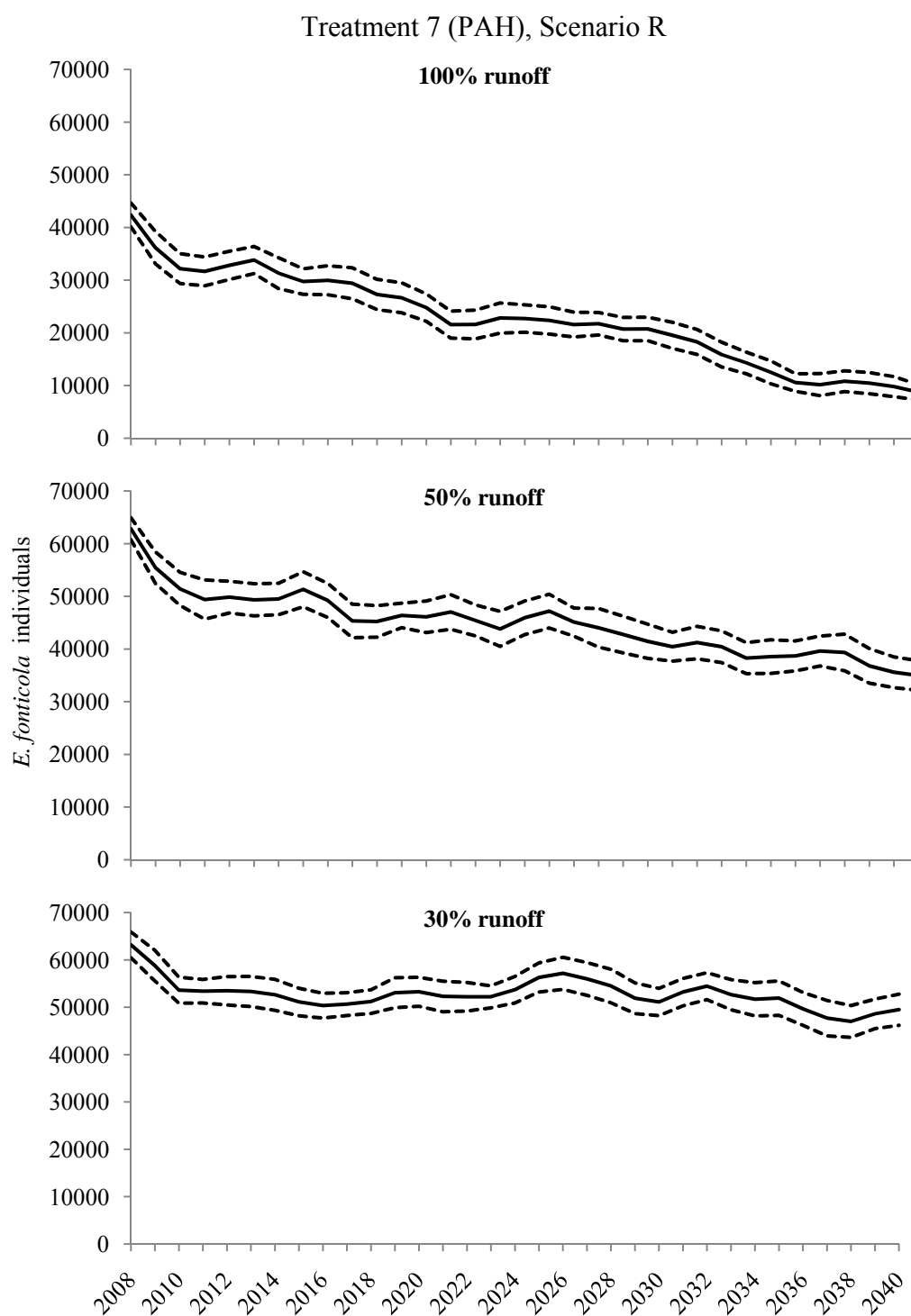


Fig. 33. Annual mean populations of *E. fonticola* modeled with phenanthrene in the water, a stochastic springflow and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

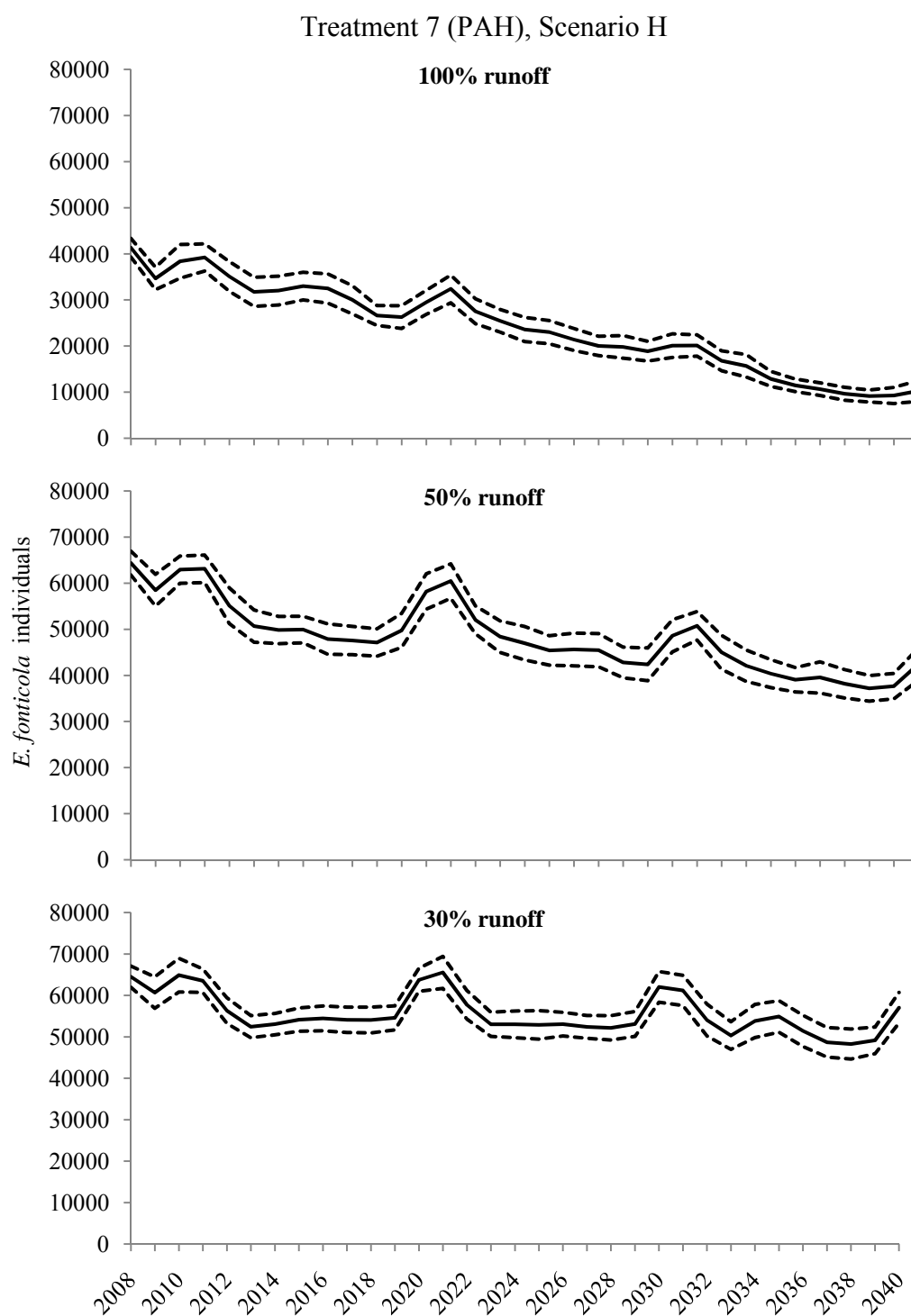


Fig. 34. Annual mean populations of *E. fonticola* modeled with phenanthrene in the water, a stochastic springflow with forced high flow years and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

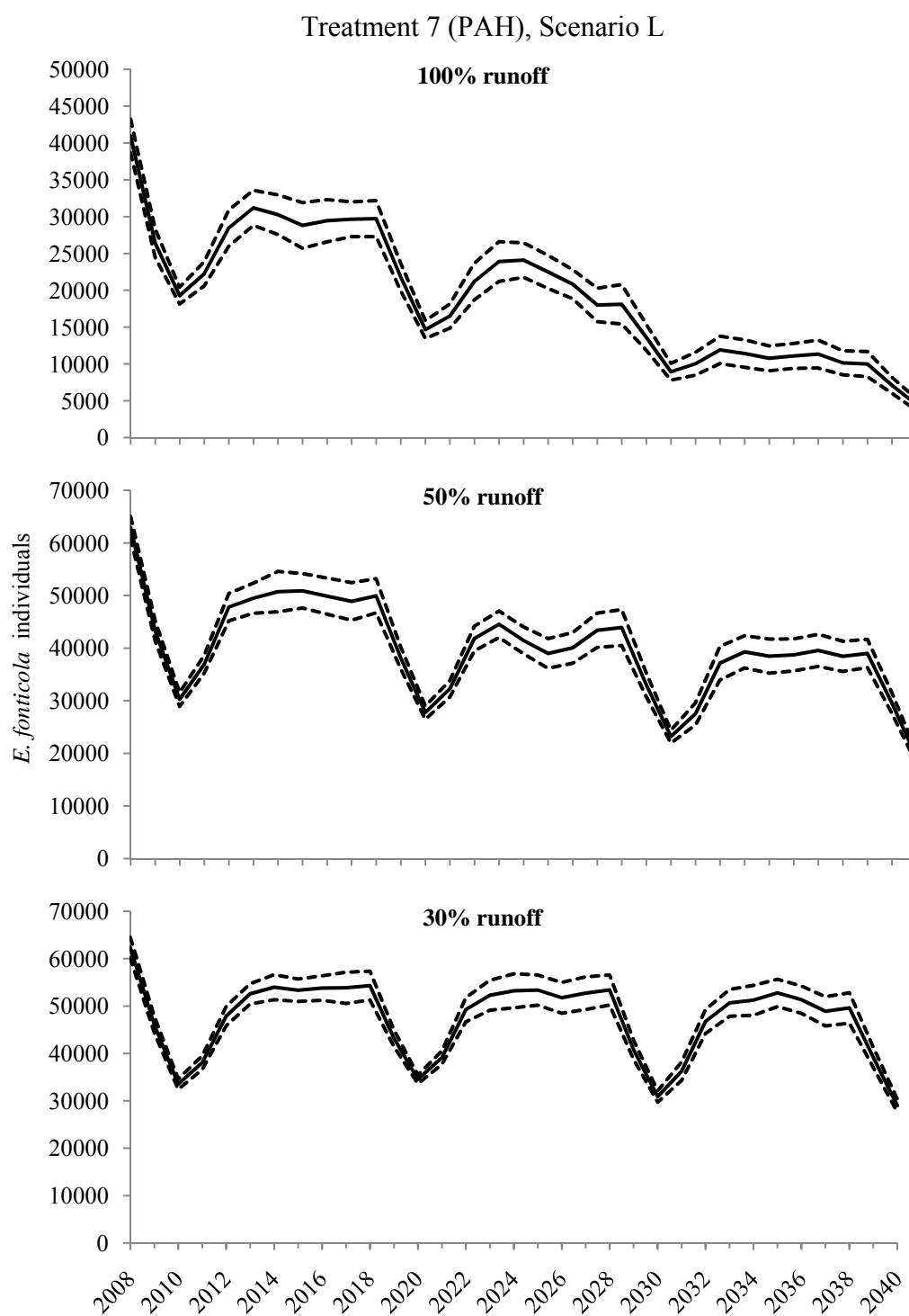


Fig. 35. Annual mean populations of *E. fonticola* modeled with phenanthrene in the water, a stochastic springflow with forced low flow years and varying percent of runoff entering the system. Dotted lines represent 95% confidence level of the mean.

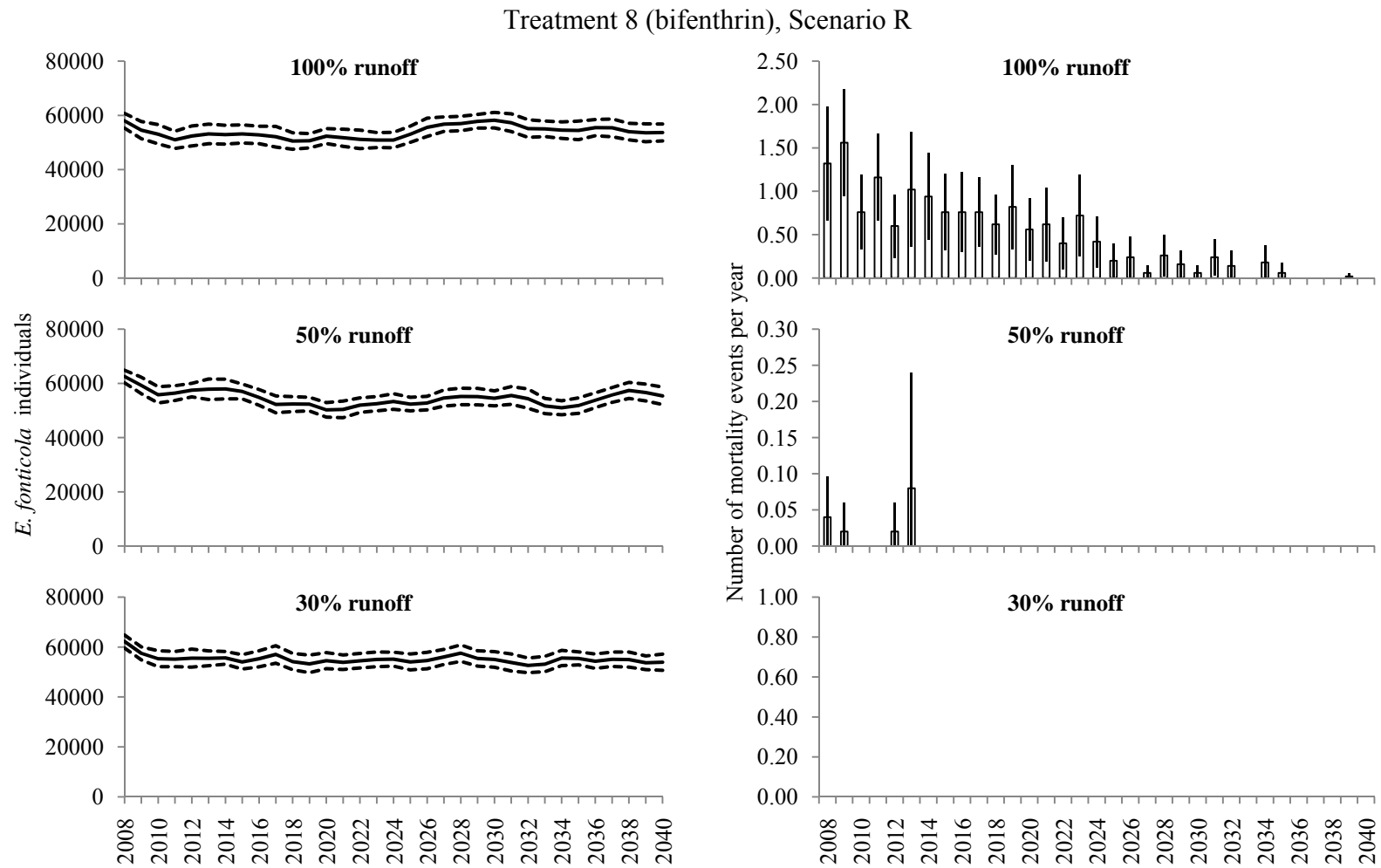


Fig. 36. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved bifenthrin exceeded acute mortality levels (4 day average of 0.15 µg/L) (right column) for treatment 8-R. Model conditions: bifenthrin, stochastic springflows, and variation on percentage of runoff entering the San Marcos River.

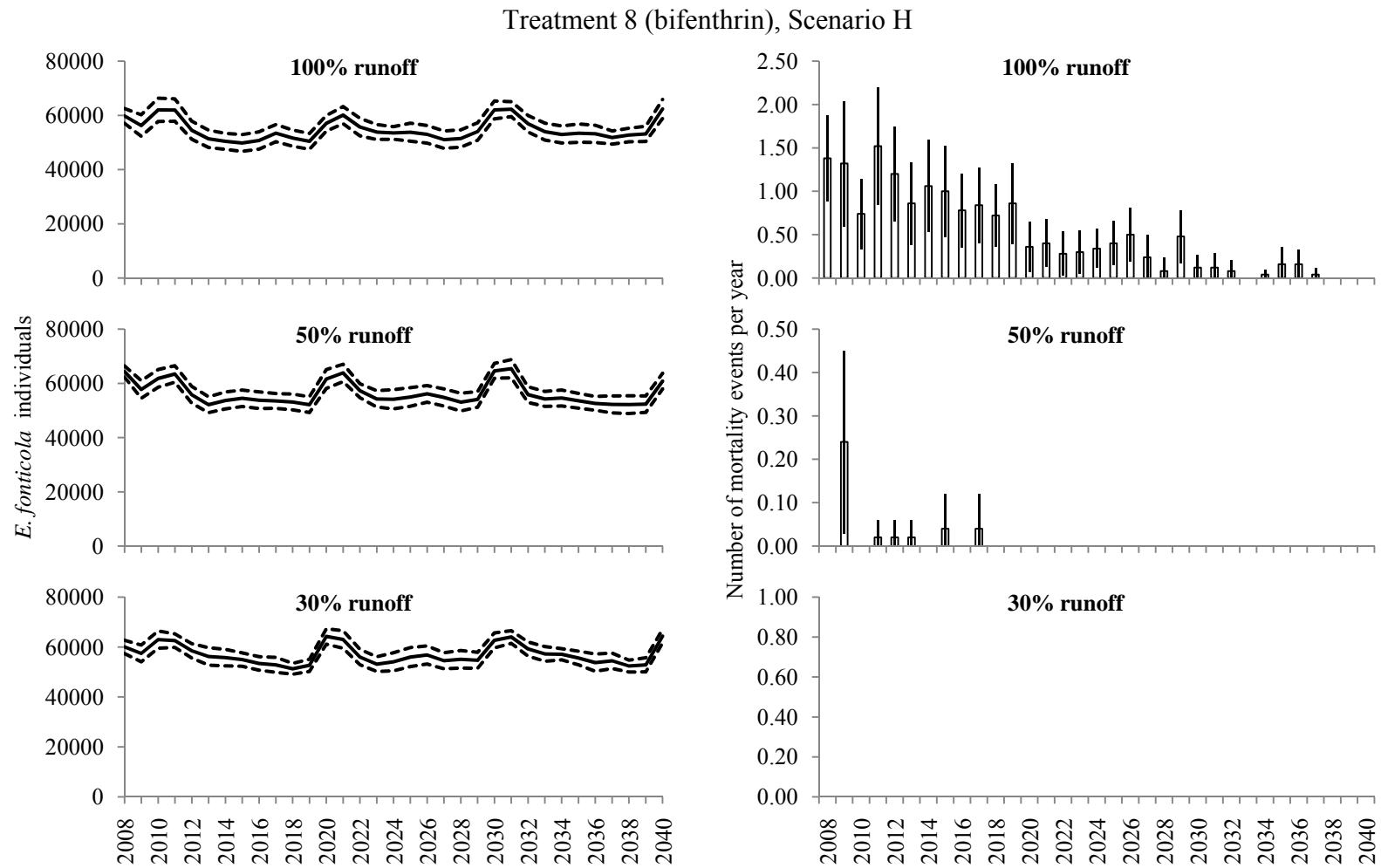


Fig. 37. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved bifenthrin exceeded acute mortality levels (4 day average of 0.15 $\mu\text{g/L}$) (right column) for treatment 8-H. Model conditions: bifenthrin, stochastic springflows except at forced high flow years, and variation on percentage of runoff entering the San Marcos River.

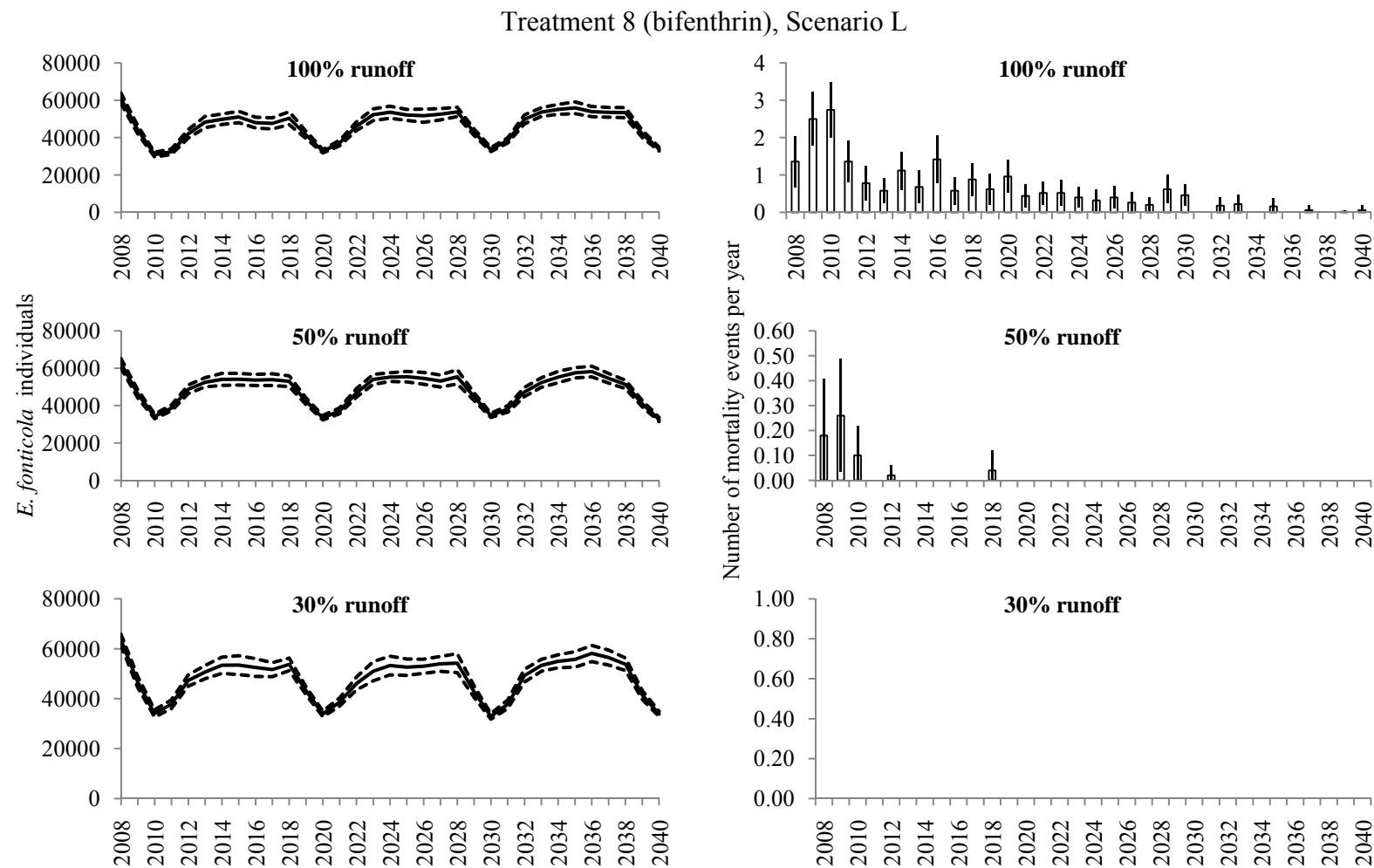


Fig. 38. Annual mean population of *E. fonticola* (dotted line = 95% CI) (left column) and the average number of times levels of dissolved bifenthrin exceeded acute mortality levels (4 day average of 0.15 $\mu\text{g/L}$) (right column) for treatment 8-L. Model conditions: bifenthrin, stochastic springflows except at forced low flow years, and variation on percentage of runoff entering the San Marcos River.

Mortality events

Since phenanthrene toxicity was modeled in a different manner than the other three organics, no mortality events per year were calculable. However, of the pesticides, bifenthrin was the only one to exceed concentration protection levels set for aquatic life under situations where 100 % runoff entered the river. Under this situation, the concentration of bifenthrin was exceeded an average of number of > 1 time per year from 2008–2014 and < 0.5 times per year from 2020 and beyond (Fig. 36-38).

Simulated last day and minimum population values

I tested if the simulated populations as of December 31, 2040 and the minimum populations under organic toxicity were significantly lower than the values simulated under clean water conditions (Chapter II) (Table 12). From paired t -tests ($\alpha = 0.05$, $df = 49$), I determined that clean water conditions resulted in a significantly larger last day population across each scenario for phenanthrene: R-100 ($t=28.178$, $p<0.000$), R-50 ($t=9.956$, $p<0.000$), R-30 ($t=3.529$, $p=0.001$), H-100 ($t=26.666$, $p<0.000$), H-50 ($t=10.398$, $p<0.000$), H-30 ($t=2.77$, $p=0.008$), L-100 ($t=46.815$, $p<0.000$), L-50 ($t=17.997$, $p<0.000$) and L-30 ($t=7.054$, $p<0.000$). For bifenthrin, carbaryl and dicamba, the last day populations were not significantly different from that of the clean water treatment.

In clean water, minimum values were significantly larger than all phenanthrene scenarios: R-100 ($t=34.946$, $p<0.000$), R-50 ($t=18.012$, $p<0.000$), R-30 ($t=5.805$, $p=0.001$), H-100 ($t=35.901$, $p<0.000$), H-50 ($t=12.482$, $p<0.000$), H-30 ($t=3.217$, $p=0.002$), L-100 ($t=48.184$, $p<0.000$), L-50 ($t=20.109$, $p<0.000$) and L-30 ($t=6.222$, $p<0.000$). Dicamba and carbaryl had no affect and neither did bifenthrin but for scenarios R-100 ($t=2.625$, $p=0.012$) and L-100 ($t=3.33$, $p=0.002$).

Table 12

Exposed to organics, mean (SD) *E. fonticola* population values on simulated December 31, 2040 (last day) and lowest daily population (minimum) over the simulated period (2008–2040).

Scenario ^a	Bifenthrin		PAHs	
	Last day	Minimum	Last day	Minimum
R – 100	32306 (7249)	17973 (3111) *	4622 (3360) *	2363 (1558) *
R– 50	32982 (7673)	19680 (2746)	19675(7033) *	10191 (2355) *
R – 30	32568 (7026)	19189 (2864)	28167 (8442) *	15917 (3449) *
H – 100	41817 (7540)	18561 (2774)	6540 (4982) *	2269 (969) *
H– 50	40411 (6217)	19260 (2552)	26619 (6817) *	12006 (2618) *
H–30	42952 (5485)	19459 (3042)	37269 (8219) *	16732 (3754) *
L–100	19424 (1974)	14436 (2002) *	2003 (1634) *	1457 (1004) *
L–50	18543 (2515)	15692 (2153)	10279 (2429) *	8544 (1448) *
L–30	19521 (1773)	15267 (2107)	15936 (2550) *	13420 (2490) *

^a R,H, L corresponds to simulated flow condition (random, high, low) respectively and 100,50,30 corresponds to the simulated percentage of runoff expected to reach the river.

* Values significantly lower than that of corresponding values in conditions of uncontaminated water.

CHAPTER V

DISCUSSION

To determine how one of the endangered species within the Edwards Aquifer might react to future urbanization and the associated levels of toxic pollutants, I developed a computer simulation model. As with any model, there were assumptions that I needed to make about the system-of-interest. However, after development and evaluation, the model simulated heavy metal and organic toxicity impacts on the darter population within the Upper San Marcos River into the future, as land use of the watershed is expected to increase in its percentage of imperviousness. Results suggest that should runoff not be managed for heavy metals or hydrocarbons, the darter population is susceptible to a decline. Best management practices should be implemented within the Upper San Marcos River sub-basin if not throughout the entire watershed basin and aquifer region. For without these in place, water quality, especially around growing cities within the boundaries of the aquifer, could decrease in integrity and compromise not only the fountain darter but also the other endemic aquatic species.

Model assumptions

Within every model there are assumptions to be made about its system-of-interest. I had to make assumptions about 1) future springflows, 2) aquatic life criteria, 3) runoff and contamination concentrations and 4) land use associations.

The underlining assumption made for this model was that springflow levels of the future will be within the ranges of the past. Flow rates at the San Marcos Spring depends upon the water demand within the entire Edwards Aquifer region. Agricultural pressures or increased withdrawal from groundwater wells outside the modelled sub-basin's boundaries can decrease the level of flow at the spring (Keplinger et al., 1998). And although the Edwards Aquifer is rechargeable, overexploitation could be harmful to aquatic organisms as springflow is related to habitat condition; a reduction of flow changes habitat conditions (USFWS, 1995; Custodio, 2002). But requirements of springflow have been set above 100 cfs to prevent take of fountain darters within the San

Marcos River (USFWS, 1995) and Senate Bill 1477 has mandated that pumping within the aquifer be restricted to 400,000 acre-ft per year (Votteler, 1998). Therefore, the model simulates future springflow as replicates of the past.

A second assumption within the model is that rainbow trout toxicity tests for zinc, cadmium, chromium phenanthrene, bifenthrin and dicamba are representative of the aquatic life criteria for fountain darters. As an endangered species, selective toxicity tests have been performed on fountain darters (i.e., copper and carbaryl). However, to simulate toxicity impacts on the darters for the other contaminants of interest I needed to determine an adequate surrogate species. Toxicity tests have shown that fountain darters are as or more sensitive than the trout despite the fact that the darter is a warm water species and the trout a salmonid, cold water species (Dwyer et al., 2005). Therefore, I used rainbow trout (early-life stage) toxicity test results as base-level aquatic life criteria for the fountain darters for chemicals modeled other than copper and carbaryl.

The third assumption relates to contaminant concentration in runoff. Research shows that the concentration of pollution in runoff declines as the duration of a rain event continues, with the greatest concentration being at the start of the event (Kim et al., 2005). This is called first flush. The model does not account for this as it does not calculate duration of a rainfall event. It calculates whether it rains at time t and the quantity of the rain. This required me to assume that the concentration in runoff is the same for every rain event (EMC, event mean concentration). Using the EMC, the model generates an annual mass of contaminant (Schueler, 1987; CWP, 2003) that is applicable for watersheds like the system modeled. By this method, I was able to generate an annual quantity of pollutant mass over time that could be then proportioned out to daily mass and from which, calculate the daily concentration within the river.

Lastly, the fourth assumption that I made, is that future pesticide application will decline as the area of total pervious surfaces are expected to decline over time. The model does not differentiate between the different types of pervious surfaces, such as agricultural land, lawn, forest etc. but models that the inverse proportion of land not developed (impervious) is subject to pesticide application. As this area becomes

smaller over time, the model simulates that application will decline. In future applications of the model, this would need to be reevaluated to account for changes of land use within pervious surfaces such as change from forest (limited applications likely) to lawns, where applications occur.

Simulation models are mathematical reconstructions that incorporate the ecological processes and parameters deemed valuable in solving a research problem. Conclusions are available under the constraints of the assumptions made, but with a clear understanding of those assumptions, the results of the model can be extremely informative.

Model results and implications

Regardless of model uncertainties, the simulated results suggest that should levels of urban related pollutants be left unchecked in the Upper San Marcos River sub-basin, the current fountain darter numbers could decline to less than 10,000 individuals by 2040 depending on what contaminant dominates the water quality. Under the assumption that 100 or even 50 percent of available runoff enters the San Marcos River, the model simulated that as of 2008 the concentration of dissolved copper, zinc, cadmium and phenanthrene are potentially at levels that can cause mortality to the darters. But if levels of runoff are around 30 percent, the current water quality was simulated as safe but would become threatening for the darters by 2019 and beyond.

Of the 8 contaminants modeled, copper, zinc, cadmium, phenanthrene and bifenthrin all reached concentrations, either in the water or in the fish tissues, to cause mortality of the darters. Regardless of springflow or runoff, copper caused the greatest decline to the population, followed by the effects of phenanthrene and zinc. Although I assessed the individual influences of the contaminants on the darters, in the natural environment, there are additive or even synergistic affects which could compound the mortality rates and decline could occur even faster than modeled. However, in conditions of no toxicity, model results show that the fountain darter population remains stable into 2040, hovering around 54,000 individuals.

When a high flow or low flow year was simulated, regardless of water condition, the population grew or decreased, respectively. This was expected. I assumed that with a higher flow, more darter habitat is available and in a stable environment, productivity can thrive. Available habitat area related to flow is not a novel concept. In fact, it was modeled by the Institute of Natural System Engineering at Utah State University (INSE, 2004). They assessed fountain darter habitat quality (i.e., vegetation distribution) within the San Marcos River as a function of river geomorphology and flow rate (INSE, 2004). Their results showed that vegetation was minimally impacted (<10%) when springflows were maintained between 135-200 cfs (INSE, 2004). In other words, as flow approached their modeled mean flow rate (170 cfs) the habitat area available for the darters was sustained; inferring that population of darters might be more productive within this range of flow. These results are similar to the springflow parameter that I placed on the darters. In my model, as flows approached a mean flow of 175 cfs the population was less affected through modified mortality affects across life stages.

So according to the model, if the percentage of runoff expected to directly enter the river is higher than 30 percent, there is direct threat to the darters survival and recovery. The chemicals modeled that are of the most concern are two heavy metals (copper and zinc) and hydrocarbons, represented by phenanthrene.

Recommendations and model applications

Levels of the modeled contaminants within the San Marcos River are not measured at regular intervals but they are assessed for the Edwards Aquifer as a whole (EAA, 2006a). I recommend that regulatory agencies involved with protection of the Edwards Aquifer, the San Marcos River and the fountain darter take action to implement a consistent water quality testing program for the Upper San Marcos River and continue to develop best management practices (BMPs) for runoff within the watershed.

There are many techniques to divert and to treat storm water runoff (i.e., vegetation buffer, bioretention applications, filters, etc.), depending on the targeted pollutant. But all BMPs have four basic components: (1) a form of regulation that diverts runoff to a filtering substrate, (2) the initial treatment that traps large particles,

(3) the filtering media, and (4) an outflow collection of the filtered water (Claytor and Schueler, 1996). Since copper, polycyclic aromatic hydrocarbons and zinc were modeled as the most likely to cause a significant decline in the darter population, it would be important to monitor these levels but also to develop BMPs that target these species of contaminants such as sand filters. These filters have been shown to be the most effective in removing zinc, copper and PAHs for small drainage areas.

The Center for Watershed Protection in Maryland has reviewed the research regarding sand filters and found that they remove, on average, 75% of zinc, 45% of copper and 55-84% of hydrocarbons in runoff (Claytor and Schueler, 1996). A targeted approach to BMP placement would be the most ideal to capture and treat the most significant of sources. Hotspots in urban areas applicable to San Marcos include: commercial parking lots, fueling stations, industrial rooftops, outdoor storage of liquids, loading/unloading areas, and vehicle cleaning facilities (Claytor and Schueler, 1996). Therefore, I recommend that the regulating agencies involved consider the appropriate BMPs (i.e., sand filters) at these potential hotspots to treat runoff and reduce the concentration of potentially lethal chemicals entering into the San Marcos River.

Conclusions

This model was a life stage and sex based model of *Etheostoma fonticola* (fountain darters). To develop the structure, I needed detailed natural history data specific to the darters and its interactions within the Upper San Marcos River. Fortunately, critical data for model development such as natural mortality rates for each life stage (eggs, larvae, juvenile and adults) and life stage durations were available because of laboratory studies and field assessments (Brandt et al., 1993; Bonner et al., 1998). Upon development of the model, it was evaluated for its ability to simulate the population.

Simulations of the past were compared to the few available population estimates (Schenck and Whiteside, 1976; Linam, 1993) and compared against qualitative data (USFWS, 1995; Bio-West, 2006; Bio-West, 2007). Comparisons were favorable and simulation results concurred with the quantitative and qualitative sources. Should

modeling be considered for any of the other species of interest within the aquifer, I would recommend that population estimates be kept current as well as any available size class information such as duration, mortality/survival rates, sex ratios, etc. As population estimates of fountain darters are sure to be included in future field assessments, the model can be reevaluated. The parameters within this model can be updated and modified for a continual assessment of the model and the condition of the darter population.

In fact, with the appropriate data, the model as it is could be used to evaluate urbanization impacts on the Comal Spring and River system population of darters. Necessary data would include projections for the human population and total impervious area; springflow; annual and daily rainfall depths; and runoff or contaminant information for the Comal River watershed. Not only would a continual assessment of these watershed characteristics benefit the fountain darter, but also the other endangered species of the aquifer as their survival depends upon the quality and quantity of water.

There have been many models developed about the hydrology of the Edwards Aquifer to evaluate recharge and flow rates (Schulman et al., 1995; Lindgren et al., 2004; EAA, 2006b) but none have directly modeled one of its species of concern. The INSE model provided insight into flow ranges that might be most suitable for darter habitat but they do not attempt to provide population estimates for the species (INSE, 2004). Research regarding any of the endangered or threatened species within the aquifer has been restricted to field or laboratory assessments. Specifically, fountain darter assessments to date have focused on flow and habitat conditions (i.e., vegetation structure, river morphology) in the Comal and San Marcos Rivers (Saunders et al., 2001; HES, 2004; Bio-West, 2006; Bio-West, 2007). And although the US Fish and Wildlife Service have set water quality criteria for endangered aquatic species (White et al., 2006), there has been no effort to model potential future water quality conditions of the San Marcos River.

The fountain darter has a recovery priority of 5C, which means that there is a “high degree of threat, a low recovery potential” and that its recovery efforts “may be in

conflict with construction or development projects” (USFWS, 1995). Up until now, there has not been any effort to project what recovery might be for the fountain darter under such urban constraints. The model developed for this research is the first to assess recovery potential for the darters specifically, the first to attempt to identify and quantify potential water quality contaminants in the San Marcos region and the first to model an endangered Edward Aquifer species. Results show that urbanization will in fact have an impact on the darter but that its influence is related to the amount of runoff allowed into the system. May its results be used by regulating agencies to develop targeted best management practices within the sub-basin or even extend to the entire aquifer region to mitigate water quality changes, as urban centers are sure to continue to expand.

CHAPTER VI

SUMMARY

As human population increases, there are land use changes that have the potential to modify the Edwards Aquifer of south-central Texas. Projections of population growth and subsequently urban area as indicated by total impervious area for Hays County are available, but before now there was no synthesis of the data to forecast possible impacts on the endangered species within the San Marcos river system. Using a population dynamics model constructed in STELLA 7.0.1® for Windows®, I was able to incorporate such data and assess urbanization impacts on *Etheostoma fonticola* within the Upper San Marcos River.

Within the model, San Marcos' human population and total impervious area drive annual runoff and determine the input of heavy metals and organics into the San Marcos River to 2040. Springflow and rainfall determine the river's concentrations of such water quality parameters. Fountain darter larvae are susceptible to mortality should levels go beyond a specified aquatic life criterion. The metals and organics that had an impact on the modeled population were copper, zinc, cadmium, phenanthrene and bifenthrin. Assuming that 30% of expected runoff enters the river directly, within the next ten years, metals could potentially be a problem within the San Marcos River and PAHs might already be at harmful levels. Low flow exacerbated the declines, as there is less water for the contaminant mass to dissolve. At conditions of 100% and 50% runoff entering the river, there was an increase in average mortality events per year. However, with effectively no contamination or and low levels of runoff the darter population was held steady around 54,000 individuals. This suggests that a reduction of storm water runoff can prevent accumulation of harmful contaminants in aquatic systems and that declines to the darter population due to urbanization can be mitigated.

Agencies involved with management of the fountain darters need to incorporate into their assessments the quantity and quality of the runoff that directly enters the San Marcos River. Sand filters can help to mitigate for runoff at pollution hotspots such as parking lots or I-35. Best management practices within the city of San Marcos need to

be evaluated and monitoring of storm water pollutants need to be developed so that the water quality within the San Marcos River can be upheld for the sustainability of the darters.

With a decrease in water quality, not only could the darters be adversely affected but the overall river system or even aquifer would be impacted should rates of contamination be similar across urban areas of the aquifer. This would threaten not only the fountain darter but also the San Marcos salamander, the Comal Springs dryopid beetle, the Comal Springs riffle beetle, the Peck's cave amphipod, or the Texas blind salamander. Declines in these populations due to urbanization might be averted should regulating agencies take into consideration the results of the model and institute BMPs across the Edwards Aquifer but especially in urban centers like San Marcos.

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APPENDIX A**MODELED DAILY RAINFALL PROPORTIONS (2000-2007).**

Table 13
Modeled daily rainfall proportions (2000-2007).

Day	2000	2001	2002	2003	2004	2005	2006	2007
1-Jan	0	0	0	0	0.0004	0	0	0
2-Jan	0	0	0	0	0	0.0062	0	0
3-Jan	0	0	0	0	0	0.0054	0	0.0287
4-Jan	0	0	0	0	0	0	0	0.0012
5-Jan	0	0	0.0134	0	0	0.0031	0	0
6-Jan	0	0	0	0	0.0004	0	0	0.0002
7-Jan	0.0566	0.0007	0	0	0	0.0009	0	0
8-Jan	0.0052	0	0	0	0.0008	0.0004	0	0
9-Jan	0	0	0	0	0.0002	0	0	0
10-Jan	0	0.0379	0	0	0	0	0	0
11-Jan	0	0	0	0.0097	0	0	0	0
12-Jan	0	0.0005	0	0.0334	0	0.0054	0	0.0005
13-Jan	0	0.0002	0	0	0	0	0	0.0538
14-Jan	0	0.0002	0	0	0.0004	0	0	0.016
15-Jan	0	0	0	0.0004	0.0163	0	0	0.039
16-Jan	0	0.0005	0	0.0012	0.023	0	0	0
17-Jan	0	0.0045	0	0	0	0	0	0.012
18-Jan	0	0.009	0	0	0	0	0	0.0055
19-Jan	0	0.0005	0.0002	0	0	0	0	0.0007
20-Jan	0	0	0	0	0	0.0004	0	0.0062
21-Jan	0	0	0	0.0004	0	0	0.0004	0.0005
22-Jan	0	0	0	0	0	0.0004	0.0064	0
23-Jan	0	0	0	0	0	0	0	0.0072
24-Jan	0	0	0.0002	0	0.0114	0	0	0.0072
25-Jan	0	0.0002	0	0.0008	0.0011	0	0	0
26-Jan	0	0	0	0.0051	0	0	0	0
27-Jan	0.0092	0.0076	0	0.0004	0	0.054	0	0
28-Jan	0	0.0047	0	0	0	0.0085	0.0102	0
29-Jan	0	0.0024	0	0.0004	0.0004	0	0	0
30-Jan	0	0	0	0	0	0	0	0.0005
31-Jan	0	0	0	0	0	0.0004	0	0
1-Feb	0.0002	0	0	0	0	0.0442	0	0.0012
2-Feb	0.0257	0	0.0002	0	0	0.0004	0.0004	0
3-Feb	0	0	0	0	0	0	0	0
4-Feb	0	0	0.0004	0	0.008	0	0	0
5-Feb	0	0	0.0123	0	0.0002	0	0	0
6-Feb	0	0	0	0.0066	0	0.0107	0	0
7-Feb	0	0	0	0.0051	0	0.0517	0	0
8-Feb	0	0.0002	0	0	0	0.0004	0	0.0002
9-Feb	0	0.0005	0	0.0039	0.0135	0	0	0
10-Feb	0	0	0	0.0023	0.0049	0	0.0057	0
11-Feb	0	0.0009	0	0	0.0108	0	0	0
12-Feb	0	0.0005	0	0	0.0002	0.0009	0	0.0024
13-Feb	0	0	0	0	0.0008	0.004	0	0
14-Feb	0	0.0002	0	0.0012	0.0025	0	0	0
15-Feb	0	0.0005	0	0.0016	0	0	0	0
16-Feb	0	0.0208	0	0.0019	0	0	0	0
17-Feb	0	0	0	0	0	0	0.003	0
18-Feb	0	0	0	0	0	0	0.0008	0
19-Feb	0	0	0.0004	0	0	0.0031	0.0004	0
20-Feb	0	0	0	0.0023	0.0008	0	0.0027	0
21-Feb	0.0005	0	0	0.0711	0	0.0009	0.0015	0
22-Feb	0.0209	0	0	0.0074	0	0	0	0
23-Feb	0.0145	0.0014	0	0	0.0008	0	0	0
24-Feb	0	0	0	0	0.0085	0.0232	0	0.0002
25-Feb	0	0	0	0.0097	0	0	0.0099	0
26-Feb	0.0065	0	0	0.0039	0	0.0245	0.0015	0
27-Feb	0	0.0002	0	0.0016	0	0.0004	0	0.0002
28-Feb	0	0	0	0	0.0028	0	0	0.0002
1-Mar	0	0.0002	0	0.0004	0	0	0	0
2-Mar	0	0.0083	0.0006	0.0039	0.0028	0	0	0.0007
3-Mar	0	0.0142	0.0002	0.0214	0.0011	0	0	0
4-Mar	0	0.0012	0	0.0074	0.0146	0	0	0

Table 13 Continued

Day	2000	2001	2002	2003	2004	2005	2006	2007
5-Mar	0	0	0	0	0.0008	0	0	0
6-Mar	0	0	0	0.0004	0	0.0714	0	0
7-Mar	0.0005	0	0	0	0	0.0054	0	0
8-Mar	0	0.0024	0	0	0	0	0	0
9-Mar	0	0	0	0	0	0	0	0
10-Mar	0	0	0.0006	0	0	0	0	0
11-Mar	0	0.0007	0.0006	0	0	0	0	0
12-Mar	0	0.0121	0.0004	0.0004	0.0021	0	0	0.0598
13-Mar	0	0.0009	0	0	0.0084	0	0.0004	0.0124
14-Mar	0.0077	0.0118	0	0	0.0009	0	0	0.0359
15-Mar	0	0	0	0	0	0	0	0.0002
16-Mar	0.01	0	0	0	0.0015	0.0045	0	0.0012
17-Mar	0.0366	0.0007	0	0	0.0002	0.0062	0.0011	0
18-Mar	0	0.0059	0	0.0004	0	0	0	0
19-Mar	0.0005	0.0009	0.0004	0.0008	0.0002	0	0.0019	0
20-Mar	0	0	0.0175	0	0.0002	0	0	0
21-Mar	0.001	0	0.0004	0	0.0019	0	0	0
22-Mar	0	0	0	0	0	0.0071	0	0
23-Mar	0	0	0	0.0004	0	0	0.0057	0
24-Mar	0	0.0002	0	0	0.0002	0	0	0
25-Mar	0	0	0	0	0	0	0	0
26-Mar	0.0007	0	0	0.0089	0	0	0	0
27-Mar	0	0.0118	0	0	0	0.0103	0.0091	0.0445
28-Mar	0	0.0002	0	0	0	0	0.0133	0.0002
29-Mar	0	0.0007	0	0	0.0008	0	0	0
30-Mar	0	0	0	0	0	0	0	0.0017
31-Mar	0	0.0005	0.0009	0	0	0	0	0.0041
1-Apr	0.0002	0	0	0	0	0	0	0
2-Apr	0.0102	0	0	0	0.0061	0	0	0
3-Apr	0.0217	0	0	0	0	0	0	0
4-Apr	0	0.0002	0	0	0.0139	0	0	0.0158
5-Apr	0	0	0	0	0	0.0116	0	0
6-Apr	0	0	0.0013	0.0019	0	0.0004	0	0
7-Apr	0	0	0.026	0.0008	0.0008	0	0	0.0036
8-Apr	0	0	0.0074	0	0	0	0	0.0213
9-Apr	0	0	0	0	0	0	0	0
10-Apr	0	0	0	0	0.018	0	0	0.0012
11-Apr	0.0002	0.0047	0	0	0.0051	0.0004	0	0
12-Apr	0.0242	0	0	0	0	0	0	0
13-Apr	0.0002	0	0	0	0	0	0	0.005
14-Apr	0	0	0	0	0	0	0	0.0055
15-Apr	0	0	0	0	0	0	0	0
16-Apr	0	0	0.0011	0.0016	0	0	0	0
17-Apr	0	0.0005	0	0	0	0	0	0.0048
18-Apr	0	0	0	0	0	0.0045	0	0
19-Apr	0	0	0	0	0	0	0	0
20-Apr	0	0	0	0.0012	0	0	0.0675	0
21-Apr	0	0	0	0	0	0	0.0288	0
22-Apr	0	0	0	0.0027	0	0.0049	0	0.001
23-Apr	0	0.0455	0	0	0	0	0	0
24-Apr	0	0.0043	0	0	0.0053	0	0	0.0005
25-Apr	0	0	0.0002	0	0	0.0089	0	0.0194
26-Apr	0	0	0.0002	0	0.0028	0.0004	0.0038	0
27-Apr	0	0	0	0	0	0	0	0
28-Apr	0	0	0	0	0	0	0	0
29-Apr	0	0	0	0	0.0015	0	0.0512	0.0018
30-Apr	0	0	0	0	0	0.0156	0	0.0081
1-May	0.0409	0	0	0	0.0129	0	0	0.0024
2-May	0.0611	0	0	0	0	0	0	0.0084
3-May	0	0	0	0	0	0.0004	0	0
4-May	0.0075	0.0099	0	0	0	0.0018	0	0.012
5-May	0	0.0346	0	0	0	0	0.044	0
6-May	0	0.0448	0	0	0	0	0.0114	0
7-May	0	0	0	0.0016	0.0013	0	0.0402	0
8-May	0	0	0	0	0	0	0.0004	0

Table 13 Continued

Day	2000	2001	2002	2003	2004	2005	2006	2007
9-May	0.0002	0	0	0	0	0.0294	0	0.012
10-May	0	0	0	0	0.0002	0	0	0
11-May	0	0.0002	0	0.0023	0.0038	0	0	0
12-May	0.0065	0.0118	0	0.0027	0.0013	0	0	0
13-May	0.0032	0	0.0045	0	0.0201	0	0	0
14-May	0.0002	0.0002	0	0	0.0123	0.0058	0.0011	0
15-May	0	0	0	0	0	0	0	0
16-May	0	0	0	0	0	0.0134	0	0.0239
17-May	0	0	0	0	0	0.0009	0	0
18-May	0	0	0	0	0	0	0	0
19-May	0.0354	0	0	0	0	0	0	0
20-May	0.0037	0	0	0	0	0	0	0.001
21-May	0.0012	0.0306	0	0	0	0	0	0.0014
22-May	0	0	0	0	0	0	0	0.0172
23-May	0	0	0	0	0	0	0	0
24-May	0	0.0014	0	0	0	0	0	0.0077
25-May	0	0.0002	0	0	0	0	0	0.0007
26-May	0	0	0.0022	0	0	0.0178	0	0.0017
27-May	0.0002	0	0	0	0	0	0	0.0167
28-May	0	0	0.0299	0	0	0.0067	0.0042	0.0007
29-May	0	0	0.0117	0	0	0.0361	0.0061	0
30-May	0	0	0	0	0	0.0486	0	0
31-May	0	0.0189	0	0	0.0004	0	0	0
1-Jun	0	0.0002	0	0	0	0.0321	0.0102	0
2-Jun	0.0047	0	0	0	0	0	0	0
3-Jun	0.0062	0	0	0.0416	0.0089	0	0	0.0115
4-Jun	0.0015	0	0	0	0	0	0	0.0048
5-Jun	0.0027	0	0	0.0311	0.0332	0	0	0
6-Jun	0	0	0	0.0455	0	0	0	0
7-Jun	0.0022	0	0	0.0012	0.0279	0	0	0
8-Jun	0.0045	0.0031	0	0	0.0101	0.0076	0	0
9-Jun	0.013	0	0.0043	0	0.0399	0	0	0
10-Jun	0.0638	0	0	0.0047	0	0	0	0
11-Jun	0.0309	0	0	0	0.0006	0	0	0
12-Jun	0.001	0	0	0	0	0	0	0
13-Jun	0.0002	0	0	0	0.0008	0	0	0
14-Jun	0.0002	0	0	0.042	0	0	0	0.0024
15-Jun	0	0.0002	0	0.0183	0.0055	0	0	0
16-Jun	0.0012	0	0.0171	0.0008	0	0	0	0.0206
17-Jun	0.0002	0	0	0	0	0	0.0554	0.0184
18-Jun	0.0105	0	0	0	0.0004	0	0.025	0
19-Jun	0.0025	0	0	0	0	0	0	0
20-Jun	0	0	0	0	0	0.0013	0	0.0263
21-Jun	0	0	0	0	0	0	0	0.006
22-Jun	0	0	0	0	0.0046	0	0	0.0053
23-Jun	0	0	0	0	0	0	0	0.0053
24-Jun	0	0.0583	0	0	0.0027	0	0	0
25-Jun	0	0	0	0	0.0076	0	0	0
26-Jun	0	0	0.0152	0	0	0	0	0
27-Jun	0	0	0.0002	0	0.0063	0	0	0.0012
28-Jun	0	0	0	0	0.0114	0	0	0.01
29-Jun	0	0	0.008	0	0.0171	0	0	0
30-Jun	0	0	0.0867	0	0.0205	0	0.0015	0
1-Jul	0	0.0486	0.0277	0	0	0	0	0
2-Jul	0	0.0005	0.0756	0	0	0	0.0004	0.0005
3-Jul	0	0.0069	0.0236	0	0	0	0.0023	0.0072
4-Jul	0	0	0	0.0198	0	0	0	0.0256
5-Jul	0	0	0.013	0.0175	0	0	0.0717	0.0079
6-Jul	0	0	0.0004	0.0035	0	0.0004	0.0004	0.0263
7-Jul	0	0	0.0093	0	0	0.0169	0	0.0012
8-Jul	0	0	0.0039	0.0206	0	0.0004	0	0.0163
9-Jul	0	0	0.0006	0.0012	0	0	0	0
10-Jul	0	0	0	0.0016	0	0	0	0
11-Jul	0	0	0	0	0.0021	0	0	0
12-Jul	0	0	0	0	0	0	0	0

Table 13 Continued

Day	2000	2001	2002	2003	2004	2005	2006	2007
13-Jul	0	0	0.0069	0	0	0	0	0
14-Jul	0	0	0.0093	0	0	0.0049	0	0.0002
15-Jul	0	0	0.0065	0.0047	0	0.0245	0	0.0022
16-Jul	0	0	0.0195	0.0012	0	0.0607	0	0.0005
17-Jul	0	0	0.0084	0	0	0.0268	0	0.001
18-Jul	0	0	0	0	0	0	0	0.0203
19-Jul	0	0	0	0	0	0	0	0.0017
20-Jul	0	0	0	0	0	0	0	0.0727
21-Jul	0	0	0	0	0	0.0009	0	0.0077
22-Jul	0	0	0	0	0	0	0	0
23-Jul	0.0005	0	0	0	0	0	0.0049	0.0026
24-Jul	0	0	0	0.0008	0	0.0045	0	0.0132
25-Jul	0	0	0	0	0.0237	0	0	0.0139
26-Jul	0	0	0	0.0008	0	0	0	0.0017
27-Jul	0	0	0	0.0019	0	0	0.0011	0
28-Jul	0	0	0	0.0132	0	0.0004	0	0
29-Jul	0	0	0	0.0004	0	0	0	0.0005
30-Jul	0.0005	0	0	0	0	0	0	0.0017
31-Jul	0.009	0	0	0	0	0	0	0.0005
1-Aug	0	0	0	0	0	0	0	0
2-Aug	0	0	0	0	0	0	0	0
3-Aug	0	0	0	0	0	0	0	0
4-Aug	0	0	0	0	0	0	0.0011	0.0002
5-Aug	0	0	0	0	0	0	0	0
6-Aug	0	0	0	0	0	0	0.0023	0
7-Aug	0	0	0	0	0.0002	0	0	0
8-Aug	0	0	0.008	0.0008	0	0.0312	0	0
9-Aug	0.011	0	0	0	0	0	0	0
10-Aug	0	0	0.0013	0.0004	0	0.0004	0	0
11-Aug	0	0	0.0002	0.0093	0.0015	0	0	0
12-Aug	0	0	0	0.0012	0	0	0	0
13-Aug	0	0	0	0.0085	0	0	0	0
14-Aug	0	0	0	0	0	0	0	0
15-Aug	0	0	0	0	0	0	0	0
16-Aug	0	0	0	0	0	0	0	0.0033
17-Aug	0	0	0	0	0	0	0	0.0191
18-Aug	0	0	0	0	0	0	0	0.0091
19-Aug	0	0	0	0	0	0.0013	0	0
20-Aug	0	0	0	0	0	0	0	0
21-Aug	0	0	0	0	0	0	0	0
22-Aug	0.0002	0	0	0	0.0046	0	0	0
23-Aug	0	0	0	0	0.0013	0	0	0
24-Aug	0	0	0	0	0	0	0	0
25-Aug	0	0	0	0	0	0	0	0.0005
26-Aug	0	0.0258	0	0	0	0	0	0
27-Aug	0	0.0261	0	0	0	0	0	0
28-Aug	0	0.0189	0	0	0.0302	0	0	0
29-Aug	0	0.0296	0.0108	0	0	0	0.0114	0
30-Aug	0	0.0711	0	0	0	0	0.0004	0.0029
31-Aug	0	0.0088	0	0.0144	0	0	0	0.0024
1-Sep	0	0.0036	0	0.0019	0	0	0	0.0007
2-Sep	0	0	0	0	0	0	0	0
3-Sep	0	0.0014	0	0.0023	0	0.0013	0	0.0022
4-Sep	0	0	0	0	0	0	0	0.0002
5-Sep	0	0.0279	0	0	0.0019	0	0.0303	0.0041
6-Sep	0	0.0005	0	0	0	0	0	0
7-Sep	0	0.0005	0.0461	0	0.0376	0	0	0
8-Sep	0	0	0.0054	0	0	0	0.0046	0
9-Sep	0.0154	0.0002	0.0199	0	0	0	0.0023	0
10-Sep	0	0	0.0002	0.0039	0	0	0	0
11-Sep	0	0	0	0.174	0	0.0022	0.0175	0.0151
12-Sep	0.0017	0	0	0.0229	0	0.0196	0.0038	0
13-Sep	0.0002	0	0	0.0004	0	0	0	0
14-Sep	0.0341	0	0	0.0194	0.0082	0	0	0
15-Sep	0	0	0.0004	0	0.0209	0	0	0.001

Table 13 Continued

Day	2000	2001	2002	2003	2004	2005	2006	2007
16-Sep	0	0	0.0013	0	0	0	0	0
17-Sep	0	0	0	0.0016	0	0	0.0186	0
18-Sep	0	0	0	0.014	0	0	0.0175	0.0007
19-Sep	0	0	0.0152	0.0155	0	0	0	0
20-Sep	0	0	0	0.0291	0	0	0	0
21-Sep	0.0027	0.0002	0	0.0008	0	0	0	0
22-Sep	0	0.0211	0	0	0	0	0	0
23-Sep	0	0.0007	0	0	0	0	0	0
24-Sep	0.0122	0	0	0	0	0	0	0
25-Sep	0.0002	0	0	0	0	0	0	0
26-Sep	0	0	0	0.0062	0.0004	0	0	0
27-Sep	0	0	0	0	0	0	0	0
28-Sep	0	0	0	0	0	0	0.0008	0
29-Sep	0	0	0	0	0	0	0	0.0012
30-Sep	0	0	0	0	0	0	0	0
1-Oct	0	0	0.0009	0	0	0	0	0
2-Oct	0	0	0	0	0.0382	0	0	0
3-Oct	0	0	0	0	0.012	0	0	0
4-Oct	0	0	0	0	0.0059	0	0	0
5-Oct	0	0.0005	0	0	0	0	0	0
6-Oct	0.0025	0	0	0.0039	0	0	0	0
7-Oct	0.0257	0	0.0403	0	0	0.0054	0	0
8-Oct	0.0189	0	0.0702	0.0008	0	0	0	0.0084
9-Oct	0.006	0	0.0011	0.0039	0.0004	0	0	0
10-Oct	0	0	0	0	0	0.041	0	0
11-Oct	0	0.0012	0	0.0699	0	0.0566	0.0417	0
12-Oct	0	0.0133	0	0.0008	0	0	0.0011	0
13-Oct	0	0.0329	0.0009	0	0	0	0	0
14-Oct	0	0	0.0061	0.0008	0.0285	0	0	0
15-Oct	0.0015	0	0.0004	0	0.0009	0	0.0038	0
16-Oct	0	0	0	0	0	0	0.0019	0
17-Oct	0.0067	0	0	0	0	0	0.0042	0
18-Oct	0.0002	0	0	0	0	0	0	0
19-Oct	0	0.0002	0.0193	0	0	0	0.1305	0
20-Oct	0	0	0	0	0	0	0.0023	0
21-Oct	0.0311	0	0.003	0	0	0	0	0
22-Oct	0.0444	0	0.0108	0	0	0	0	0.0115
23-Oct	0.0025	0	0.0191	0	0.0342	0	0	0
24-Oct	0.0102	0	0.0318	0	0.0209	0.0022	0	0
25-Oct	0.0002	0	0.0152	0	0.0042	0	0	0
26-Oct	0	0	0.0004	0.0078	0.0004	0	0.0288	0
27-Oct	0	0	0.0004	0	0.0015	0	0	0
28-Oct	0	0	0.0011	0	0	0	0	0
29-Oct	0	0	0.0006	0	0	0	0	0
30-Oct	0	0	0	0	0	0	0	0
31-Oct	0	0	0	0	0	0.0187	0	0
1-Nov	0.0075	0	0	0	0.0313	0	0.0004	0
2-Nov	0.0037	0	0	0.0004	0.0002	0	0	0
3-Nov	0.0748	0	0.0119	0.0008	0	0	0	0
4-Nov	0.0015	0	0.0113	0	0	0	0	0
5-Nov	0	0	0.0737	0	0	0	0	0
6-Nov	0	0	0	0	0	0	0.0008	0
7-Nov	0	0	0	0.0008	0	0	0	0
8-Nov	0	0	0	0	0	0	0	0
9-Nov	0	0	0	0.0004	0	0	0	0
10-Nov	0	0	0	0	0.0002	0	0	0
11-Nov	0.0025	0	0.0002	0.0004	0	0	0	0
12-Nov	0.0012	0	0	0	0	0	0	0
13-Nov	0	0	0	0	0	0	0	0
14-Nov	0	0.0005	0	0	0.0063	0	0	0
15-Nov	0	0.0694	0	0.0008	0.0074	0	0	0
16-Nov	0.0012	0.0045	0	0	0.0457	0	0	0
17-Nov	0.003	0.0002	0	0.0587	0.0634	0	0	0.0007
18-Nov	0.0224	0	0	0	0.0002	0	0	0.0048
19-Nov	0.01	0.0092	0	0	0	0	0	0

Table 13 Continued

Day	2000	2001	2002	2003	2004	2005	2006	2007
20-Nov	0	0	0	0	0.0065	0	0	0
21-Nov	0	0	0	0	0.0271	0	0	0
22-Nov	0	0	0	0.0004	0.0661	0	0	0.0014
23-Nov	0.0179	0	0	0	0.0068	0	0	0
24-Nov	0.0311	0	0	0	0	0	0	0.0055
25-Nov	0	0	0	0	0	0	0	0.0167
26-Nov	0	0	0.0002	0	0	0.0691	0	0
27-Nov	0	0.0002	0.0035	0.0004	0.0002	0	0	0
28-Nov	0	0.036	0	0	0	0	0	0
29-Nov	0	0.0057	0	0	0	0	0.0053	0
30-Nov	0	0	0	0	0.0104	0	0.008	0
1-Dec	0.0005	0.0007	0	0	0	0	0	0
2-Dec	0	0.0142	0	0	0	0	0	0
3-Dec	0.0062	0.0005	0.0065	0	0	0	0	0
4-Dec	0	0	0.0217	0	0	0.0004	0	0
5-Dec	0	0	0	0	0	0	0	0
6-Dec	0	0	0	0	0	0	0	0
7-Dec	0	0	0	0	0.0009	0.0031	0	0
8-Dec	0	0.0272	0.0115	0	0	0.0004	0	0
9-Dec	0	0	0.0221	0.0004	0	0	0	0
10-Dec	0.0002	0	0.0002	0	0.0002	0	0.0008	0
11-Dec	0	0.0218	0.0004	0	0	0	0	0.0007
12-Dec	0.0002	0	0.0084	0.0113	0	0	0.0008	0.0014
13-Dec	0.0007	0.0059	0	0.0004	0	0	0	0
14-Dec	0	0	0	0	0	0.0013	0	0.0029
15-Dec	0.0002	0.0246	0	0.0004	0	0	0	0.0072
16-Dec	0	0.0019	0	0	0	0.0009	0	0
17-Dec	0	0	0.0002	0	0	0.0004	0	0
18-Dec	0	0	0	0	0	0	0	0
19-Dec	0	0	0	0	0	0	0	0
20-Dec	0	0	0	0	0	0	0.0015	0
21-Dec	0	0	0	0	0	0	0.0076	0
22-Dec	0	0	0.0039	0	0	0	0	0
23-Dec	0.0005	0	0.0139	0	0.0006	0	0.0895	0
24-Dec	0.0025	0	0	0	0	0	0.03	0
25-Dec	0	0	0	0	0	0	0	0
26-Dec	0.0125	0	0	0	0	0	0	0.0002
27-Dec	0	0	0	0.0004	0	0	0	0.0005
28-Dec	0	0	0	0.0085	0	0	0	0.0002
29-Dec	0	0	0	0	0	0	0.0095	0
30-Dec	0	0	0.0093	0	0	0	0.0148	0
31-Dec	0.0025	0	0.0004	0	0.0002	0	0.0004	0

(NOAA, San Marcos, 2000-2007)

APPENDIX B

MODELED METAL AND PHENANTHRENE RUNOFF EVENT MEAN

CONCENTRATIONS ($\mu\text{g/L}$)

Table 14
Modeled metal and phenanthrene runoff event mean concentrations ($\mu\text{g/L}$).

Year	Cd ^a	Cr ^a	Cu ^a	Zn ^a	PAH ^b	Year	Cd ^a	Cr ^a	Cu ^a	Zn ^a	PAH ^b
1973	0.61	3.54	11.85	141.50	6.83	2008	0.82	4.75	15.89	189.76	7.17
1974	0.61	3.56	11.92	142.32	6.83	2009	0.83	4.83	16.16	193.02	7.19
1975	0.62	3.58	11.99	143.14	6.84	2010	0.85	4.91	16.44	196.28	7.21
1976	0.62	3.60	12.05	143.96	6.84	2011	0.86	4.99	16.70	199.48	7.23
1977	0.62	3.62	12.12	144.79	6.85	2012	0.87	5.07	16.97	202.68	7.26
1978	0.63	3.64	12.19	145.61	6.85	2013	0.89	5.15	17.24	205.88	7.28
1979	0.63	3.66	12.26	146.43	6.86	2014	0.90	5.23	17.51	209.09	7.30
1980	0.63	3.68	12.33	147.25	6.87	2015	0.92	5.31	17.78	212.29	7.33
1981	0.64	3.70	12.40	148.07	6.87	2016	0.93	5.39	18.04	215.49	7.35
1982	0.64	3.72	12.47	148.89	6.88	2017	0.94	5.47	18.31	218.69	7.37
1983	0.65	3.75	12.54	149.71	6.88	2018	0.96	5.55	18.58	221.89	7.39
1984	0.65	3.77	12.60	150.54	6.89	2019	0.97	5.63	18.85	225.09	7.42
1985	0.65	3.79	12.67	151.36	6.89	2020	0.98	5.71	19.12	228.29	7.44
1986	0.66	3.81	12.74	152.18	6.90	2021	1.00	5.82	19.48	232.59	7.47
1987	0.66	3.83	12.81	153.00	6.91	2022	1.02	5.93	19.84	236.90	7.50
1988	0.66	3.85	12.88	153.82	6.91	2023	1.04	6.03	20.20	241.20	7.53
1989	0.67	3.87	12.95	154.64	6.92	2024	1.06	6.14	20.56	245.50	7.56
1990	0.67	3.89	13.02	155.46	6.92	2025	1.08	6.25	20.92	249.80	7.59
1991	0.67	3.91	13.09	156.29	6.93	2026	1.10	6.36	21.28	254.10	7.62
1992	0.68	3.93	13.16	157.11	6.94	2027	1.11	6.46	21.64	258.41	7.65
1993	0.68	3.95	13.22	157.93	6.94	2028	1.13	6.57	22.00	262.71	7.68
1994	0.68	3.97	13.29	158.75	6.95	2029	1.15	6.68	22.36	267.01	7.71
1995	0.69	3.99	13.36	159.57	6.95	2030	1.17	6.79	22.72	271.31	7.74
1996	0.69	4.01	13.43	160.39	6.96	2031	1.19	6.93	23.20	277.09	7.78
1997	0.69	4.03	13.50	161.21	6.96	2032	1.22	7.08	23.69	282.88	7.82
1998	0.70	4.05	13.57	162.04	6.97	2033	1.24	7.22	24.17	288.66	7.86
1999	0.70	4.07	13.64	162.86	6.98	2034	1.27	7.37	24.65	294.44	7.91
2000	0.71	4.09	13.71	163.68	6.98	2035	1.29	7.51	25.14	300.22	7.95
2001	0.72	4.18	13.98	166.94	7.00	2036	1.32	7.66	25.62	306.00	7.99
2002	0.73	4.26	14.25	170.20	7.03	2037	1.34	7.80	26.11	311.78	8.03
2003	0.75	4.34	14.52	173.46	7.05	2038	1.37	7.94	26.59	317.57	8.07
2004	0.76	4.42	14.80	176.72	7.07	2039	1.39	8.09	27.07	323.35	8.11
2005	0.78	4.50	15.07	179.98	7.10	2040	1.42	8.23	27.53	329.13	8.15
2006	0.79	4.58	15.34	183.24	7.12						
2007	0.80	4.67	15.62	186.50	7.14						

^a CWP, 2003

^b Menzie et al., 2002

VITA

In the Sunshine State, Leann Irene Wilkins received her Bachelor of Science degree in Environmental Science with a focus of Conservation Biology and Landscape Ecology in 2005 from University of Miami, Florida. She then spent two years volunteering within the two largest states of the nation. Although she came face to face with North America's largest mammals canoeing through miles of Alaskan rivers and hiking through the Kenai, the Texas Attwater's Prairie Chickens found a special place in her heart. As Texas took a hold of her, Leann enrolled in the Wildlife and Fisheries Department at Texas A&M University in August 2007. In May 2009, she became the first grandchild of the Wilkins clan to receive a Master of Science. Her research interests include human dimensions of wildlife management, endangered species conservation and urban biology. Her permanent address is 210 Nagle Hall, WFSC, Texas A&M University, College Station, Texas 77843-2258. She may also be contacted at leann_wilkins@tamu.edu.